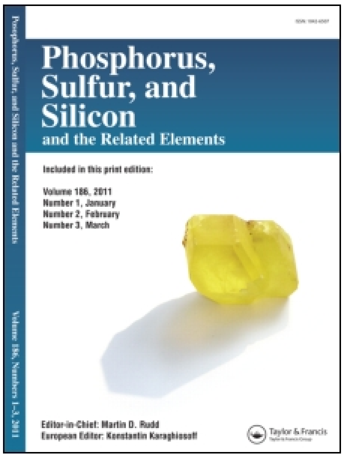

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REACTIVITY OF O,O-DIETHYLDITHIOPHOSPHORIC ACID TOWARDS DIFFERENT ETHYLENIC SYSTEMS

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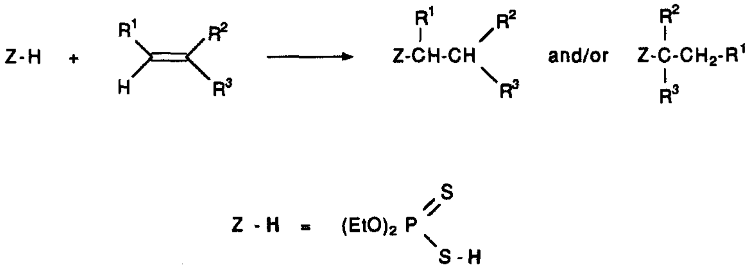
Reactions of O,O-diethyldithiophosphoric acid [$(EtO)_2P(S)$-SH] with different alkenes or heterosubstituted alkenes are presented and discussed.

Key words: Phosphorodithioic acids; trialkylthionophosphates; cycloalkenes; alkenes; thioethers; ^{13}C NMR; ^{31}P NMR.

INTRODUCTION

The chemistry of dithiophosphoric acids has been extensively investigated because many of the adducts are important oil additives[1] and insecticides.[2] We now report our preliminary work concerning the reactivity of dithiophosphoric acids with (hetero) substituted alkenes.[3,4] It was interesting to clarify the regioselectivity of this addition regarding the degree of substitution of the alkene and/or the presence of some heteroatoms. Due to our laboratory specialty, the latter are essentially represented by oxygen and sulfur. The reaction is shown below (Scheme I) and consists on refluxing the dithiophosphoric acid (Z-H) with the ethylenic's compound at 80–100°C during ten hours, without any solvent and catalyst.

The starting material is O,O-diethyldithiophosphoric acid. This compound was chosen because it is readily available from P_4S_{10} and EtOH,[5] and easy to purify.[6]

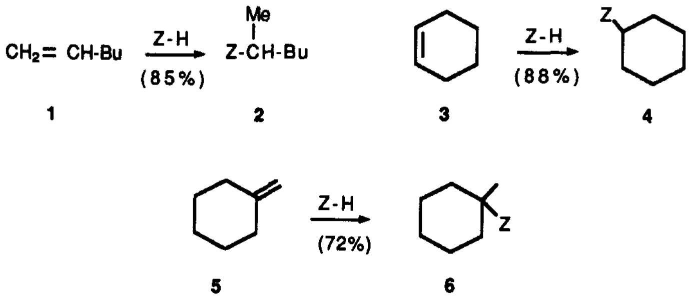


SCHEME I

RESULTS AND DISCUSSION

1. Reaction of Simple Alkenes

When simple alkenes are treated with O,O-diethyldithiophosphoric acid (Scheme II), good to excellent yields of the addition products are observed. The reaction products are the result of the "Markovnikov" rule,[7] classical addition[8] of **Z-H**, without any carbocationic rearrangement, as shown with 1-hexene (**1**), cyclohexene (**3**), and methylene cyclohexane (**5**).

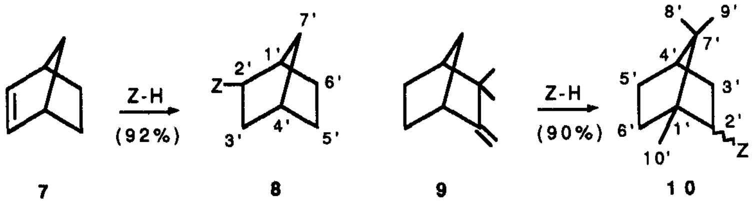


SCHEME II

2. Reactivity of Bicyclic Olefins

The same results were obtained with the double bond in a bicyclic system (Scheme III). The most notable feature of the results appears in the case of (±)β-camphene (**9**), the carbocationic rearrangement of this being exactly like when it's treated in strong acid-catalyzed reaction.[9]

We can make the following remarks: From compound **7**, the addition is stereoselective: compound **8** is obtained only in exo form. At the contrary, compound **10** is obtained in the two forms, endo and exo in 1/1 molar ratio. The C13 NMR shows that some carbons of the mixture have the same chemical shift, but always, **C1′** and **C2′** can be differentiated in the two forms (see Table I). (Note: Most of δ have been assigned by the PS's method.[10])



SCHEME III

3. Reactivity of Alkenes Containing an Heteroatom

When the heteroatom is not directly attached to one of the ethylenic carbons, it is found that the reaction's orientation varies with the type of alkenes used (Scheme

TABLE I

13C and 31P NMR (non aromatic compounds) spectroscopic data

	13C	13C	13C	13C	13C	13C	13C	13C	31P
N°	C-Z	C	C	C	C	C/Me	C/Me	C/Me	
2	45,7 J=4,0	37,8 J=7,3	29,0	22,4		23,1 J=8,4	13,8		94,4
4	48,3 J=3,7	34,8 J=5,7	25,8	25,2					94,8
6	39,6 J=6,6	25,3	22,3	22,3		29,6			94,9
8	C2' 49,7 J=3,9	C1' 44,2 J=4,1	C3' 40,3 J=8,0	C4'/5' 36,4 28,6	C6'/7' 28,1 35,7				93,5
10	C2' 55,8 55,6	C1'/4' 49,8 49,6 46,1	C3' 38,3	C5' 27,1	C6' 41,7 41,5	C7' 47,5	C8'/9' 20,4 20,3 19,9	C10' 14,2	95,3
14	40,1 J=3,6	116,5 CN	26,6 J=3,6 CH2-CN			21,4 J=8,6			90,8
34	56,3 J=5,8	36,4 J=6,2				29,1 J=5,4	8,9		93,6
38	24,5 J=3,7	46,6 J=2,9 CH2-SO2				57,8 C/t.Bu		22,9 Me/t.Bu	90,2
40	28,8 J=3,8	117,3 CN	19,2 J=3,2 CH2-CN						93,6

• Chemical shifts of Z (CH2 and CH3) are discussed in the text.

IV). So, (meth) allylic systems behave like simple linear olefins and the results observed are the same as in **1**) following "Markovnikov" addition without any carbocationic rearrangement.

Typical examples are shown below:

$$CH_2{=}CH{-}CH_2{-}S{-}Ph \xrightarrow[(62\%)]{Z{-}H} Z{-}CH(Me){-}CH_2{-}S{-}Ph$$

11 **12**

$$CH_2{=}CH{-}CH_2{-}CN \xrightarrow[(81\%)]{Z{-}H} Z{-}CH(Me){-}CH_2{-}CN$$

13 **14**

$$CH_2{=}C(Me){-}CH_2{-}X{-}Ph \xrightarrow{Z{-}H} Z{-}C(Me)_2{-}CH_2{-}X{-}Ph$$

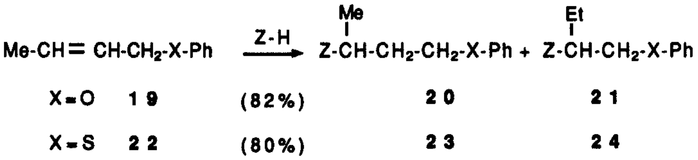
X=O **15** (70%) **16**

X=S **17** (65%) **18**

SCHEME IV

The results are different with MeCH═CH— systems as represented in Scheme V. In this case, O,O-diethyldithiophosphoric acid attacks the two ethylenic carbons and the reaction product is found to contain mainly two isomers.

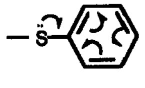
The relative yield of each seems to depend on the present heteroatom. For example, **19** gives **20** and **21** in 90% and 10% respectively, corresponding to the formation of two possible carbocations. Moreover, when sulfur is present, the ratio of the two isomers is quite different. Thus, **22** gives **23** (70%) and **24** (30%).



SCHEME V

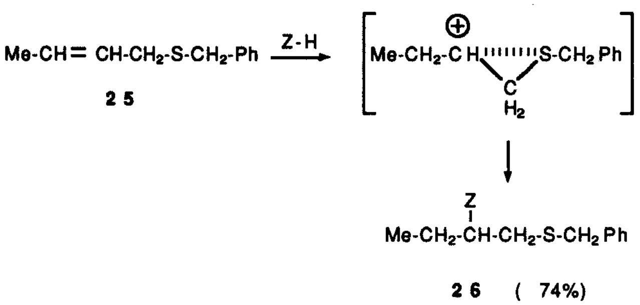
We observe that preferably the carbocation **C1** [Me—CH$^+$—CH$_2$—CH$_2$—X—Ph] with OPh and SPh is obtained.

Nevertheless, in the case of sulfur, when using benzyl group, we get opposite results with formation of the compound formed from an attack of H$^+$ upon the double bond providing the carbocation **C2** [Me—CH$_2$—CH$^+$—CH$_2$—S—CH$_2$Ph]. This shows the effect of sulfur atom or phenyl and benzyl groups. In the first case (Scheme VI), the free doublet participates in the delocalization on the aromatic ring and cannot stabilize the carbocation.[11]



SCHEME VI

In opposition, with benzyl group (Scheme VII), this doublet becomes more available and stabilizes a positive charge of the carbocation **C2**. The difference between O and S originates evidently from the different polarizabilities of these two heteroatoms.



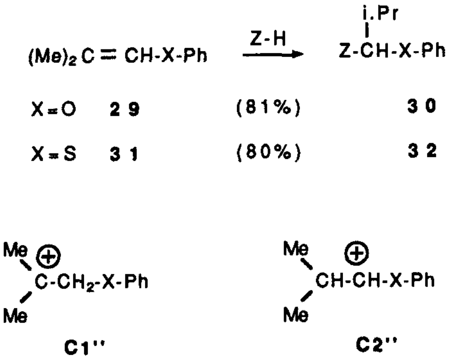
SCHEME VII

When the heteroatom is directly attached to one of the ethylenic carbons, only one isomer is obtained, resulting from a resonance stabilization of the carbocation with the unshared pair of the heteroatom.[12,13]

$$\underset{\mathbf{27}}{CH_2{=}CH\text{-}S\text{-}Ph} \xrightarrow[(83\%)]{Z\text{-}H} \underset{\mathbf{28}}{Z\text{-}CH(Me)\text{-}S\text{-}Ph}$$

SCHEME VIII

The result of the Scheme VIII is confirmed by the reaction of compounds **29** and **31**. Addition of H^+ leads to two carbocations **C1″** and **C2″**:



$$(Me)_2C = CH\text{-}X\text{-}Ph \xrightarrow{Z\text{-}H} Z\text{-}\overset{i.Pr}{\overset{|}{C}}H\text{-}X\text{-}Ph$$

X=O	**29**	(81%)	**30**
X=S	**31**	(80%)	**32**

C1″ **C2″**

SCHEME IX

C2″, because of the presence of a heteroatom, is the more stabilized form. So, **29** and **31** give only one compound each, **30** and **32**. At the opposite 2-methyl 2-butene (**33**), without a heteroatom, furnishes **34** (Scheme X) via **C1″** type carbocation.

$$\underset{\mathbf{33}}{(Me)_2C = CH\text{-}Me} \xrightarrow[(82\%)]{Z\text{-}H} \underset{\mathbf{34}}{Z\text{-}C(Me)_2\text{-}CH_2\text{-}Me}$$

SCHEME X

This reaction shows thus the influence of the heteroatom.

4. *Reactivity of Conjugated Ethylenic Compounds*

In case of activated ethylenic systems, the nucleophilic properties of the P—S group intervene. So, with a SO_2 electron withdrawing group (Scheme XI), a "Michael" type reaction takes place.

$$CH_2{=} CH\text{-}SO_2\text{-}R \xrightarrow{Z\text{-}H} Z\text{-}(CH_2)_2\text{-}SO_2\text{-}R$$

R = Ph	**35**	(78%)	**36**
R = t.Bu	**37**	(70%)	**38**

SCHEME XI

The result observed is the same in the case of acrylonitrile (Scheme XII), where the double bond is activated by a CN group.[8]

$$\underset{\mathbf{39}}{CH_2{=}CH\text{-}CN} \xrightarrow[(87\%)]{Z\text{-}H} \underset{\mathbf{40}}{Z\text{-}(CH_2)_2\text{-}CN}$$

SCHEME XII

TABLE II

13C and 31P NMR (aromatic compounds) spectroscopic data

	13C	13C	13C	13C	13C	13C	13C	13C	31P
N°	**Ar/C1'**	**Ar/C2'**	**Ar/C3'**	**Ar/C4'**	**C-Z**	**C**	**C**	**C(Me)**	
12	135,3	129,8	128,9	126,4	43,9 J=3,4	41,9 J=4,6		21,0 J=6,7	92,2
16	158,5	114,4	129,3	120,9	53,8 J=6,4	74,7 J=3,3 CH2-OPh		26,8 J=7,0	89,1
18	130,5	128,6	128,5	125,9	48,0 J=6,7	45,2		27,4 J=3,4	94,6
20	158,7	114,5	129,4	120,8	42,4 J=6,1	64,9 CH2-OPh	37,4	23,5 J=4,1	93,1
23	135,8	129,2	128,8	126,0	44,3 J=3,8	37,3 J=7,0	30,8	22,9 J=4,8	93,5
24	135,6	129,9	128,8	126,3	50,9 J=3,6	37,4 J=7,0	26,6	10,6	93,2
26	138,1	128,8	128,3	126,9	51,8 J=3,5	37,6 J=3,9	36,8 26,9 J=6,8	10,7	93,4
28	133,0	133,4	128,9	128,2	53,1 J=4,7			24,7	91,6
30	156,5	117,8	129,2	122,5	75,0	35,6 J=4,6		18,6 17,4	92,5
32	133,9	128,9	127,8	127,2	67,1 J=4,7	34,6		19,5 18,6	93,6
36	138,3	129,3	128,0	133,9	25,7 J=3,8	56,2 J=2,9			92,1

• **Chemical shifts of Z (CH2 and CH3) are discussed in the text.**

TABLE III

Refractive indexes and analytical data of the compounds prepared*

N°	n^{20}_D	Phosphorus, %		Sulfur, %	
		Calc.	Found	Calc.	Found
2	1,4909	11,45	11,39	23,72	23,79
4	1,5202	11,54	11,50	23,89	23,83
6	1,5219	10,98	11,02	22,73	22,62
8	1,5205	11,05	11,03	22,89	22,97
10	1,5285	9,61	9,50	19,90	19,95
12	1,5659	9,21	9,27	28,59	28,51
14	1,5112	12,24	12,19	25,34	25,44
16	1,5318	9,26	9,29	19,18	19,11
18	1,5604	8,84	8,92	27,45	27,73
20/21[a]	1,5545	9,26	9,13	19,18	19,27
23/24[a]	1,5456	8,84	8,68	27,45	27,66
26	1,5489	8,50	8,54	26,39	26,74
28	1,5288	9,60	9,52	29,83	29,78
30	1,5499	9,26	9,21	19,18	19,08
32	1,5192	8,84	8,89	27,45	27,53
34	1,5000	12,09	12,07	25,04	25,13
36	1,5561	8,74	8,62	27,16	27,22
38	1,5535	9,26	9,12	28,76	28,85
40	1,4999	12,95	12,91	26,82	26,90

* All the products were purified by chromatography. Decomposition of these compounds often occured during distillation.

[a] The values are given for the mixture. The two compounds have not been separated.

Registry No : 4 : [22148-27-2] ; 40 : [18205-49-7].

In conclusion, dithiophosphoric acids behave like strong acids with simple or heteroatomic alkenes, but give "Michael" adducts with conjugated double bond. In the first case, the regioselectivity of the addition is directed by the heteroatom. In addition, the synthesis method we present is interesting because it needs neither solvent nor catalyst, and can be extended to other dithiophosphoric acids and ethylenic compounds for a very good production of functionalized O,O,S-trialkylthionophosphates.[14]

EXPERIMENTAL

^{13}C NMR spectra were recorded on a BRUKER AM-400 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard.

^{31}P NMR spectra were recorded on a BRUKER AM-400 spectrometer in $CDCl_3$ using H_3PO_4 as external standard.

The chemical shifts (p.p.m) are presented in Tables I and II. We note that δC and J(PC) of $(EtO)_2P(S)$ group in the different compounds have always the same value. The averages observed are:

$\delta(CH_2)$ = 63.6 ppm; J(PC) = 6.2 Hz.
$\delta(CH_3)$ = 15.7 ppm; J(PC) = 8.4 Hz.

The elemental compositions (sulfur % and phosphorus %) and refractive indices of the products are reported in Table III.

General procedure. To 15 mmol of purified O,O-diethyldithiophosphoric acid, is slowly added dropwise at room temperature 15 mmol of the alkene. The mixture is stirred at this temperature for 30 min, then heated at 80°–100°C for 12 h.

After cooling, the mixture is poured into 50 ml of chloroform, washed with 2 × 50 ml of a solution of potassium hydroxide, and 3 × 100 ml of water. The chloroform layer is dried with sodium sulfate, filtered and the solvant removed under reduced pressure. Products are isolated by chromatography on silica gel with a mixture of pentane/ether (90–98/10-2) as eluent.

The spectroscopic data of the compounds prepared are summarized in Tables I and II, and the refractive indexes and analytical data are given in Table III.

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