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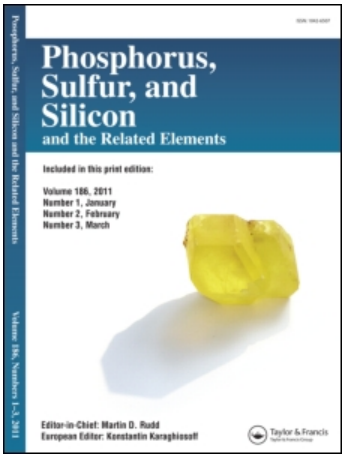

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SELECTIVE ADDITION OF O,O-DIETHYLDITHIOPHOSPHORIC ACID TO BIFUNCTIONALISED COMPOUNDS

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SELECTIVE ADDITION OF O,O-DIETHYLDITHIOPHOSPHORIC ACID TO BIFUNCTIONALISED COMPOUNDS

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O,O-diethyldithiophosphoric acid can be added selectively to activated alkenes bearing another C—C double bond or an oxirane ring. These reactions are presented and discussed.

Key words: (Meth)acrylates; phosphorodithioic acids; oxirane; trialkylthionophosphates; dicyclopentadiene, ^{13}C NMR, ^{31}P NMR.

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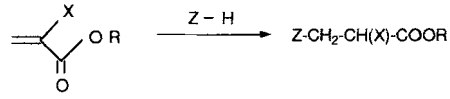
INTRODUCTION

We have recently reported our results[1] concerning the reactivity of O,O-diethyldithiophosphoric acid towards different (hetero)substituted alkenes. It was found that, according to the nature of the ethylenic compound, the addition takes place in different manners and is truly dependent on the present heteroatom.

In the case of simple conjugated ethylenic esters [(meth)acrylates], the addition of O,O-diethyldithiophosphoric acid (**Z-H**) gives a "Michaël" adduct[2] as shown below:

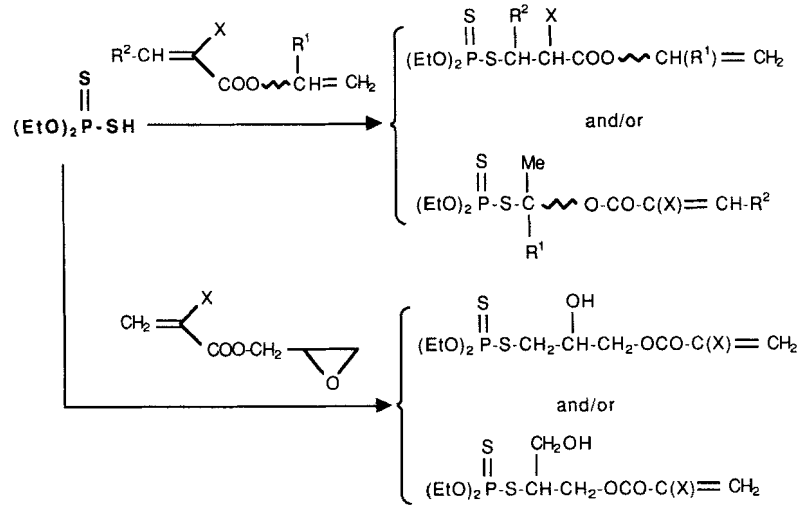


X = H ; R = Me	**1**	(84%)	**2**
X = Me ; R = Me	**3**	(79%)	**4**
X = Me ; R = CH_2Ph	**5**	(78%)	**6**

SCHEME I

Due to the presence of the methyl group, the addition to the methacrylic system compared to simple acrylates is less favored and gives lower yields. But in general, the reaction always occurs in a satisfactory way.

So, it seemed important to us to have a better approach of the behaviour and the selectivity of the dithiophosphoric acid against different competitive activated ethylenic or epoxide systems, as illustrated by Scheme II:



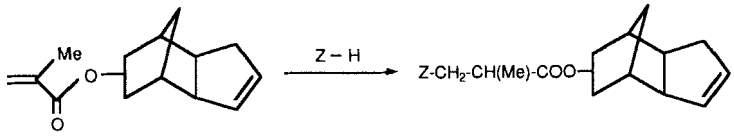
SCHEME II

The reaction consists in adding at 0°C an equimolar amount of the dithiophosphoric acid to the unsatured compound in the presence of a polymerization inhibitor agent, and then refluxing the mixture at 100–110°C during eight to ten hours.

Many of the starting ethylenic compounds are (meth)acrylic monomers[3] synthetized in this laboratory. We chose O,O-diethyldithiophosphoric acid[4] for these investigations, but the results obtained can be extended to others phosphorodithioic acids. This general type of reaction has been of interest for our work in the preparation of a variety of functionalised O,O,S trialkylthionophosphates.

RESULTS AND DISCUSSION

1) Reaction with conjugated ethylenic esters bearing another C—C double bond: Firstly, the additional on *exo-endo*-dicyclopentadienyl methacrylate[3] had been carried out as shown below:



7 (74%) 8

SCHEME III

Only compound **8**, "Michaël" adduct, was isolated.

The ^{13}C NMR spectra (Table II) showed that the ethylenic carbons of the cyclopentenyl moiety at about 132,6/132,3 p.p.m and 131,6/130,6 p.p.m (endo/exo), were retained in the adduct. This proves that exclusively the attack of **Z-H** to the conjugated ethylenic system had occurred. Differences between the reactivities of

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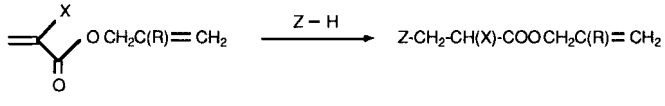
the two double bonds of the dicyclopentadiene molecule were reported in the literature. The double bond in the cyclopentene ring was found to be quite inert in the addition of various acids,[5] alcohols[6] and thiols[7] to dicyclopentadiene. This was confirmed by us. When we tried to add another molecule of O,O-diethyldithiophosphoric acid to **8**, the thionophosphate remained unchanged.

The same results were obtained with (meth)allyl (meth)acrylates,[3] where two reactive ethylenic systems are in competition. In spite of the good affinity of the dithiophosphoric acid for (meth)allylic systems, essentially the nucleophilic properties of the P(S)SH group intervened. This reveals the priority given of the addition to ethylenic conjugated systems compared to a simple activated double bond.

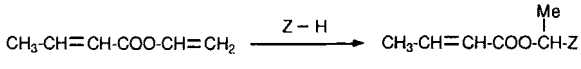
On the other hand, when the (meth)acrylic group was replaced by a crotylic system, the presence of the α-Me group prevented the "Michaël" addition as shown for crotyl vinyl ether in Scheme V. The reaction took place exclusively in the "Markovnikov" manner, and confirmed the influence of the steric enhencement in the 1, 4 addition. In this case, the vinylic double bond is priority holder. So, no terminal vinyl insaturation could be observed in the ^{13}C NMR spectra in which the crotylic system was maintained at 123,3 p.p.m (Me-$\underline{C}$H=) and 137,7 p.p.m (=$\underline{C}$H—COO—).

Secondly, the double bond had been moved further away from the conjugated ethylenic system. This may permit to have better apprehension of the selectivity



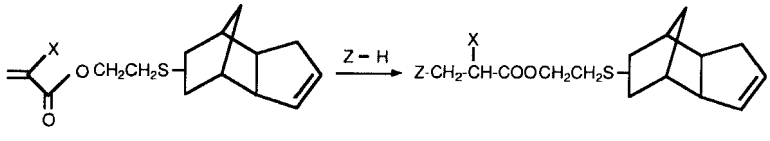
X = Me ; R = Me	**9**	(75%)	**10**
X = H ; R = Me	**11**	(81%)	**12**
X = Me ; R = H	**13**	(74%)	**14**
X = H ; R = H	**15**	(80%)	**16**

SCHEME IV



17 (70%) **18**

SCHEME V



X = H	**19**	(78%)	**20**
X = Me	**21**	(72%)	**22**

SCHEME VI

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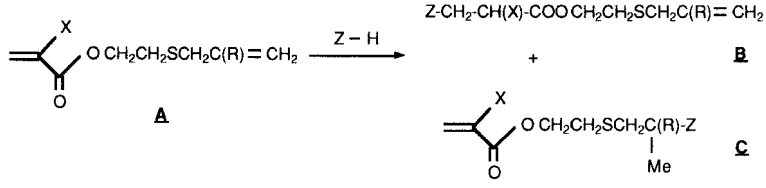
of the addition, according to the distance between the two competitive double bonds. Thus, when O,O-diethyldithiophosphoric acid was treated with **19** or **21** (mixture of endo/exo)[3], no change compared to Scheme III was noted. Once more, the pentacyclic double bond was not affected, and the "Michaël" adduct was the only isomer obtained in each instance.

Nevertheless, with acyclic compounds, the removing of the (meth)allylic system induced a decrease of the selectivity of the addition. With **23**, **26**, **29** and **32**,[3] different results varying with the substitution of the conjugated double bond, were obtained. The reaction can be illustrated by the following equation:



SCHEME VII

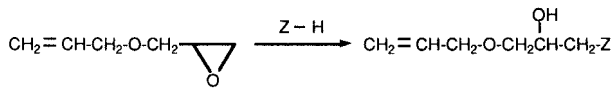
In each case, the "Michaël" adduct (**B**) remained however strongly predominating. The results are reported in Table I, in which we can observe that the ratio of the two isomers depends on the group X. When X = H, the addition on the acrylic system was more favored and logically the attack on (meth)allylic system decreased.

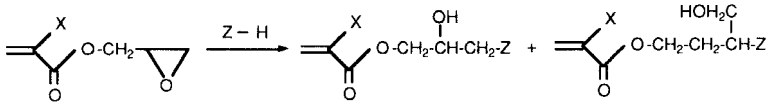
TABLE I

Ratio of the two isomers **B** and **C** (see Scheme VII)

X	R	A	B[a]	C[b]	ρ%*
Me	Me	**23**	**24**(82)	**25**(18)	65
H	Me	**26**	**27**(90)	**28**(10)	74
Me	H	**29**	**30**(84)	**31**(16)	68
H	H	**32**	**33**(91)	**34**(9)	76

a : percentage of isomer **B** in the crude mixture; b : percentage of isomer **C** in the crude mixture; * yield of the major product (**B**) after purification.





X = Me **37** (78%) **38** (96%) **39** (4%)

X = H **40** (72%) **41** (95%) **42** (5%)

SCHEME VIII

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TABLE II

$^{13}C^{a}$ and ^{31}P NMR spectra of the compounds prepared

	13C	13C	13C	13C	13C	13C	13C	13C	13C	13C	13C	31P
N°	C-Z	C	C	C	C	C	C	C=0	C=	C/Me	C/Me	
2	34,9 J=3,9	28,1 J=3,8						171,2			51,5	93,7
4	36,1 J=3,8	40,5 J=3,9						174,6		16,8	51,8	94,4
6	35,6 J=3,6	40,2 J=3,4	135,3 C1 Ar	127,7 C2 Ar	128,1 C3 Ar	128,0 C4 Ar	66,0	173,5		16,5		94,1
8[b]	36,0 J=3,7	40,6 J=4,0					77,7 77,4 CHO (DCPD)	173,7	132,6 132,3 131,6 130,6	16,8 16,7		94,3
10	36,1 J=3,8	40,4 J=4,1	66,2					173,9	140,7 113,6	16,8	20,4	94,1
12	35,2 J=3,6	28,0 J=3,8	66,0					170,8	133,8 117,0		20,5	93,9
14	36,2 J=3,8	40,7 J=4,3	65,3					173,8	131,9 118,2	16,8		94,0
16	35,0 J=3,7	28,2 J=3,8	65,2					170,5	131,7 118,2			93,7
18	76,2							164,1	146,0 121,9	17,9	23,1 J=8,0	88,2
20[c]	35,1 J=3,6	28,7 J=3,7	63,7	30,1			40,4 40,4 CHS (DCPD)	171,0	132,2 131,6 131,3 130,2			94,3
22[c]	35,0 J=3,7	40,7 J=4,0	63,6	30,2			40,4 40,4 CHS (DCPD)	173,8 31,5	132,3 16,8 131,3 130,3	16,8		94,1
24	35,0 J=3,8	40,6 J=4,1	63,2	39,4	28,9			173,8	140,7 113,9	16,8	20,4	94,2
27	35,1 J=3,9	28,2 J=3,7	63,2	39,3	29,0			170,7	140,7 113,8		20,3	93,8
30	34,9 J=3,8	40,6 J=4,3	63,2	31,1	28,9			173,9	136,0 117,3	16,8		94,0
33	34,9 J=3,8	28,1 J=3,6	63,2	31,0	30,1			170,6	136,1 117,3			93,7

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TABLE II (*Continued*)

	13C	13C	13C	13C	13C	13C	13C	13C	13C	13C	13C	31P
N°	C-Z	C	C	C	C	C	C	C=0	C=	C/Me	C/Me	
36	36,5 J=6,3	69,5	72,1	72,2					134,1 117,2			94,8
38	37,1 J=6,3	69,2	66,3					167,0	135,7 123,3	18,2		94,8
41	35,0	69,3	66,3					165,7	130,4 129,0			94,6

a : All the δC have been attribued by the PS's method.[9] Chemical shifts of **Z** (CH_2 and CH_3) are discussed in the text.

b : Mixture of endo and exo
CH (DCPD) : 54,6;51,0 / 45,7;45,7 / 42,7;41,7.
CH_2 (DCPD) : 39,0;39,0 / 38,9;38,9 / 28,7;28,7.

c : Mixture of endo and exo
CH (DCPD) : 53,0;52,0 / 47,3;45,3 / 43,0;42,1.
CH_2 (DCPD) : 38,4;38,0 / 36,0;35,8 / 32,9;31,9.

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At the opposite, with X = Me, the 1,4 addition took place with more difficulties, so the percentage of the "Markovnikov" product (**C**) increased.

2) Reaction on ethylenic systems bearing an epoxide function: Two types of epoxidated ethylenic compounds were allowed to react with O,O-diethyldithiophosphoric acid (Scheme VIII). The addition reaction, like all those carried out till now, was performed according to the same general procedure as outlined in the experimental section. In all the cases, the addition on the allylic or the conjugated double bond was disfavored and essentially the opening of the epoxide ring was noted.[8] We can make the following remarks: With allyl glycidyl ether (**35**), a regiospecific reaction was observed in which the only product formed was **36**, resulting from attack at the terminal position of the epoxide. The identification of the product was again made by investigation of the ^{13}C NMR spectra (Table II) in which, the allyl unsaturation could be observed at 117,2 p.p.m (CH_2=)/134,1 p.p.m (C<u>H</u>=), and <u>C</u>H_2-Z was detected at 36,5 p.p.m (J = 6,3 Hz).

This result is slightly different wth glycidyl methacrylate (**37**) and glycidyl acrylate (**40**) where two products were isolated in each instance. Nevertheless, the reaction exhibited a high degree of regioselectivity (**38-41**/**39-42**:96-95/4-5), in which attack by the P(S)SH group at the terminal position of the epoxide was favored. **39** and **42**, derivating from addition at the internal position of the oxirane ring, were easily detected in the mixture as a weak signal by ^{31}P NMR [95,0 p.p.m (**39**), 94,7 p.p.m (**42**)] and by ^{13}C NMR [<u>C</u>H-Z: 44,8 p.p.m (**39**)/44,6 p.p.m (**42**)].

CONCLUSION

On the basis of these results it is concluded that the addition of O,O-diethyldithiophosphoric acid to bifunctionalised derivatives, due to the duality between the

nucleophilic and electrophilic properties of the P(S)SH group, proceeds in different ways according to the two competitive functions. In summary, it is found that the addition is more facilitated with an epoxide ring than with conjugated ethylenic systems, the latter being priority holder facing (meth)allylic or simple ethylenic groups. However, when a conjugated unsaturation competes with a simple activated unsaturation, the selectivity of the reaction varies with the distance between the two double bonds and the steric enhencement of the conjugated system.

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 Table 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 and refractive indices are reported in Table III.
General procedure: To a stirred mixture of 15 mmol of purified O,O-diethyldithiophosphoric acid and 50 mg of hydroquinone monomethyl ether, is slowly added dropwise at 0°C, 15 mmol of the ethylenic compound. The solution is maintained at this temperature during 30 min, then heated at 100°–110°C for ten hours.

After cooling, the yellow residue is diluted with 50 ml of chloroform, washed with 2 × 50 ml of a solution 2N of KOH, and 3 × 100 ml of water. The chloroform phase is dried with sodium sulfate, filtered, and removed under reduced pressure to yield a crude yellow oil.

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TABLE III

Refractive indices and elemental compositions of the compounds prepared

N°	n^{20}_D	Phosphorus, % Calc.	Phosphorus, % Found	Sulfur, % Calc.	Sulfur, % Found
2	1,5024	11,37	11,41	23,55	23,62
4	1,5021	10,82	11,80	22,40	22,38
6	1,5138	8,55	8,57	17,69	17,53
8	1,5603	7,66	7,72	15,85	15,78
10	1,5028	9,49	9,44	19,65	19,73
12	1,5035	9,92	9,83	20,53	20,40
14	1,5037	9,92	9,87	20,53	20,45
16	1,5085	10,38	10,34	21,49	21,56
18	1,5051	10,38	10,29	21,49	21,65
20	1,6146	6,87	6,69	21,35	21,66
22	1,6150	6,67	6,78	20,70	20,86
24	1,5220	8,01	7,89	24,89	25,28
27	1,5224	8,31	8,45	25,82	25,91
30	1,5183	8,31	8,40	25,82	25,93
33	1,5185	8,64	8,55	26,83	27,00
36	1,5188	10,31	10,38	21,35	21,26
38/39 *	1,5225	9,43	9,39	19,53	19,61
41/42 *	1,5229	9,85	9,91	20,40	20,31

* The values are given for the mixture. The two compounds have not been separated.

Registry No : **1** : [96-33-3]; **2** : [1068-02-6]; **3** : [80-62-6]; **5** : [2495-37-6]; **15** : [96-05-9]; **17** : [14861-06-4]; **35** : [106-92-3]; **37** : [106-90-1]; **40** : [106-91-2].

The crude product is then purified by chromatography on silica gel with a mixture of pentane/ether (90/10) as eluent. All the compounds were obtained as oils. They were characterized by ^{13}C and ^{31}P NMR spectroscopy, refractive indices and combustion analyses.

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