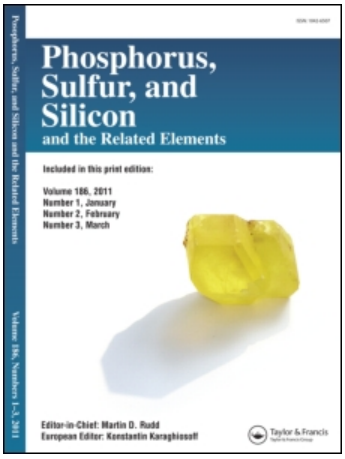


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTIVITY OF O, O'-DIALKYLDITHIOPHOSPHORIC ACID TOWARDS DIFFERENT ALLYLIC COMPOUNDS

D. Robert[a]; J. L. Mieloszynski[a]; D. Paquer[a]
[a] Laboratoire de Chimie Organique, Université de Metz, Ile du Saulcy, Metz, France

To cite this Article Robert, D. , Mieloszynski, J. L. and Paquer, D.(1994) 'REACTIVITY OF O, O'-DIALKYLDITHIOPHOSPHORIC ACID TOWARDS DIFFERENT ALLYLIC COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 97: 1, 83 — 87
To link to this Article: DOI: 10.1080/10426509408020730
URL: http://dx.doi.org/10.1080/10426509408020730

Phosphorus, Sulfur, and Silicon, 1994, Vol. 97, pp. 83–87
Reprints available directly from the publisher
Photocopying permitted by license only

REACTIVITY OF O,O'-DIALKYLDITHIOPHOSPHORIC ACID TOWARDS DIFFERENT ALLYLIC COMPOUNDS

D. ROBERT, J. L. MIELOSZYNSKI and D. PAQUER
Laboratoire de Chimie Organique, Université de Metz, Ile du Saulcy 57045 Metz, France

(Received July 12, 1994; in final form September 8, 1994)

Addition reaction of O,O'-dialkyldithiophosphoric acid with β-substituted ethylenic systems: orientation effect of the substituent.

Key words: O,O'-dialkyldithiophosphoric acid, trialkyldithiophosphoric ester, allylic compounds.

INTRODUCTION

The O,O'-dialkyldithiophosphoric acids (DTPA) are the starting materials for the preparation of compounds used in industry, specially as anti-wear and extreme-pressure additives for lubricating oil,[1–3] or as insecticides or pesticides.[4,5] We mostly focused our interest to show the influence of the "Z" substituent during the addition of DTPA to allylic systems: $CH_2{=}CH{-}CH_2{-}Z$. As a matter of fact, we established the important function of "**Z**" on the result of this reaction (Scheme I).

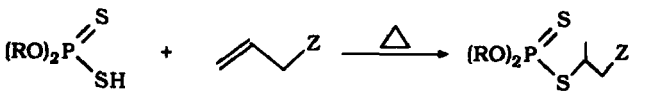
The addition of DTPA to the allylic compounds is achieved by refluxing the mixture at 80–100°C during ten hours without any solvent or catalyst.[6,7]

RESULTS AND DISCUSSION

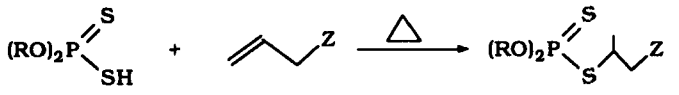
1) Reactions with $CH_2{=}CH{-}CH_2{-}Z$ Derivatives

When **1a** and **1b** DTPA are warmed with **2a–e** allylic derivatives (Scheme II), O,O,S-trialkyldithiophosphoric triesters are obtained with good yields. These products originate from a "Markovnikov"[8] addition and this selectivity is total.

Anyway in certain cases, specially with allyl iodide **3f**, the instability of the allylic derivatives leads to the polymerisation of the compound. When there is a sulfone or sulfoxide function (**2e**, **f**), the ethylenic character of the double bond decreases considerably and the electrophilic attack is no more possible.



SCHEME I

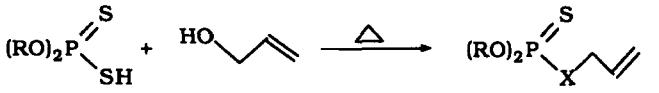


1a R = Et
1b R = t.BuS(CH$_2$)$_3$

2a Z = OEt
2b Z = SMe
2c Z = CN
2d Z = St.Bu
2e Z = SOt.Bu
2f Z = SO$_2$t.Bu
2g Z = I

3a	R = t.BuS(CH$_2$)$_3$	Z = OEt
3b	"	Z = SMe
3c	"	Z = CN
3d	R = Et	Z = CN
3e	"	Z = St.Bu
3f	R = t.BuS(CH$_2$)$_3$	Z = I
3g	R = Et	Z = SOt.Bu
3h	"	Z = SO$_2$t.Bu

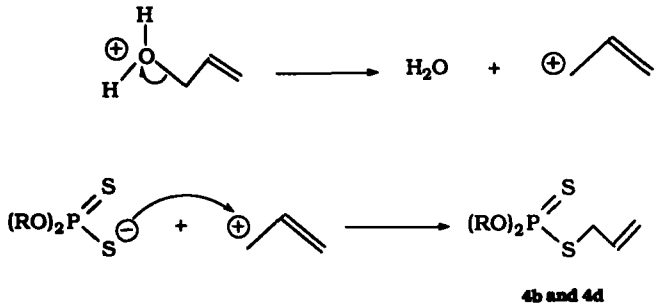
SCHEME II



1a R = Et
1b R = t.BuS(CH$_2$)$_3$

4a	R = Et ; X = O
4b	R = Et ; X = S
4c	R = t.BuS(CH$_2$)$_3$; X = O
4d	R = t.BuS(CH$_2$)$_3$; X = S

SCHEME III



4b and 4d

SCHEME IV

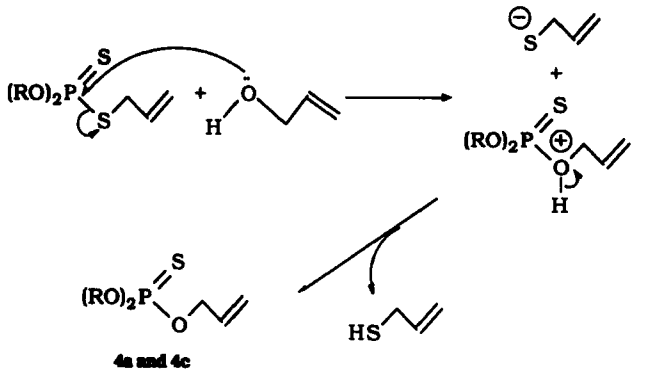
2) *Case of the Allylic Alcohol*

To obtain trialkyldithiophosphoric esters containing a hydroxyl function, we added the DTPA to the allylic alcohol according to the same procedure. However we did not obtain the expected phosphoalcohol; instead an equimolar mixture of mono and dithiophosphoric esters (Scheme III) was isolated.

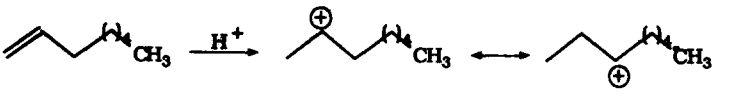
The composition of this mixture was confirmed by IC-MS and ^{31}P NMR analysis. The yields of the mixtures are 40–45% and the composition in 50% of monothiophosphoric ester and 50% of dithiophosphoric ester.

The DTPA are quite strong acids[9] and can thus protonate the hydroxyl group of allylic alcohol (Scheme IV) and produce a very stable carbocation.

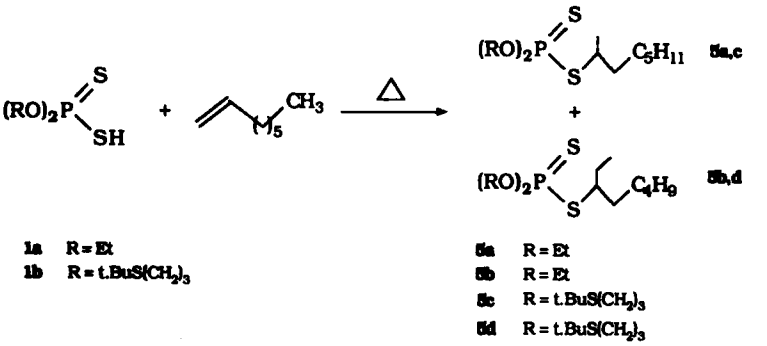
Simultaneously the oxygen atom of allylic alcohol is nucleophilic enough to substitute the "CH_2=CH—CH_2—S—" group of the dithiophosphoric ester previously formed (Scheme V).



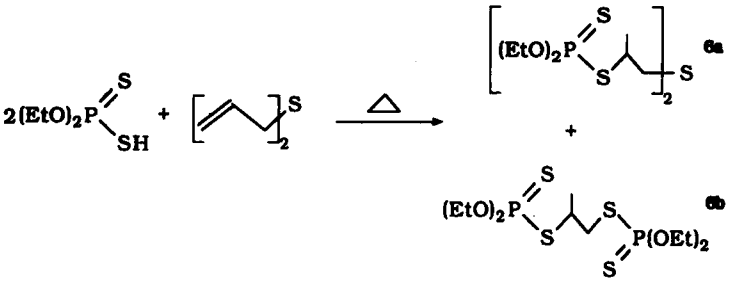
SCHEME V



SCHEME VI



SCHEME VII



SCHEME VIII

3) Case of the Octene-1

The addition of DTPA **1a** and **1b** to the octene-1 with the same conditions leads to a mixture of two phospho-triesters due to a rearrangement of the intermediate carbocation (Scheme VI).

We have two isomers whose proportions vary with the DTPA used. The relative percentages have been determined by ^{31}P NMR (Scheme VII).

4) Case of the Allyl Sulfide

The addition of two moles of DTPA leads to a mixture of two phospho-triesters. Beside the **6a** product normally expected, we also obtained the compound **6b** (Scheme VIII).

CONCLUSION

In this study we showed the influence of a "Z" substituent, on the result of the addition of DTPA to the allylic compounds. The electrophilic properties of the "P(S)SH" group, already observed during prior works,[6-9] are confirmed when the "Z" is an electron donating group. In the case of an electron withdrawing group, the double bond becomes not very reactive and the DTPA cannot react anymore. This electrophilic character is also exhibited with the octene-1 for which Wagner-Meerwein rearrangement is observed. At last in the case of phospho-triesters containing a good leaving group, a substitution can occur.

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.

General procedure. To 15 mmol of purified O,O'-dialkyldithiophosphoric 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 10 h.

After cooling, the mixture is poured into 50 ml of chloroform, washed with 3 × 100 ml of water. The chloroform layer is dried with sodium sulfate, filtered and the solvent removed under reduced pressure. Products are isolated by chromatography on silica gel with a mixture of pentane/ether (80–95/20–5) as eluent.

Compound **3a**: ^1H NMR: δ = 4.2 (m, CH_2O); 2.6 (m, SCH_2); 2.0 (m, CH_2); 1.3 (s, t.Bu); 3.5 (m, CHS); 3.6 (m, CH_2O); 1.4 (d, CH_2O); 1.2 (t, CH_3); 1.4 (d, CH_3). ^{13}C NMR: δ = 30.6 ($C(\underline{C}H_3)_3$); 41.6 ($\underline{C}(CH_3)_3$); 24.0 (SCH_2); 30.0 (CH_2, J_{CP} = 7.8); 66.2 (CH_2O, J_{CP} = 6.3); 74.2 (CH_2O, J_{CP} = 5.9); 44.0 (SCH_2); 14.7 (CH_3); 19.4 (CH_3, J_{CP} = 6.0). ^{31}P NMR: δ = 94.9. Yield = 65%.

Calcd: C 47.90; H 8.61; S 26.89; O 10.08; P 6.52.
Found: C 47.58; H 8.52; S 27.11; O 10.00; P 6.71.

Compound **3b**: ^1H NMR: δ = 4.2 (m, CH_2O); 2.6 (m, SCH_2); 2.0 (m, CH_2); 1.3 (s, t.Bu); 3.5 (m, CHS); 2.6 (m, CH_2S); 1.5 (d, CH_3); 2.2 (s, CH_3). ^{13}C NMR: δ = 30.7 ($C(\underline{C}H_3)_3$); 41.8 ($\underline{C}(CH_3)_3$); 24.1 (SCH_2); 30.1 (CH_2, J_{CP} = 7.7); 66.5 (CH_2O, J_{CP} = 6.5); 42.1 (CH_2, J_{CP} = 5.2); 44.6 (SCH_2); 16.0 (CH_3); 20.8 (CH_3, J_{CP} = 7.5). ^{31}P NMR: δ = 94.5. Yield = 78%.

Compound **3c**: ^1H NMR: δ = 4.2 (m, CH_2O); 2.6 (m, SCH_2); 2.0 (m, CH_2); 1.3 (s, t.Bu); 3.5 (m, CHS); 3.1 (m, CH_2CN); 1.4 (d, CH_3). ^{13}C NMR: δ = 116.5 (CN); 30.7 ($C(\underline{C}H_3)_3$); 41.9 ($\underline{C}(CH_3)_3$); 24.0 (SCH_2); 30.1 (CH_2, J_{CP} = 8.2); 66.8 (CH_2O, J_{CP} = 6.4); 40.3 (SCH_2, J_{CP} = 3.3); 26.7 (CH_2, J_{CP} = 4.2). 21.4 (CH_3, J_{CP} = 8.7). ^{31}P NMR: δ = 93.5. Yield = 88%.

Compound **3d**: ^1H NMR: δ = 4.2 (m, CH_2O); 1.3 (t, SCH_3); 3.6 (m, CHS); 2.9 (d, CH_2); 1.4 (dd, CH_3). ^{13}C NMR: δ = 116.6 (CN); 15.6 (Me, J_{CP} = 8.2); 64.1 (CH_2O, J_{CP} = 6.3); 40.0 (SCH, J_{CP} = 3.4); 26.6 (CH_2, J_{CP} = 4.0); 21.3 (CH_3, J_{CP} = 8.6). ^{31}P NMR: δ = 92.3. Yield = 70%.

Compound **3e**: ^{1}H NMR: δ = 4.2 (m, CH_2O); 1.3 (m, CH_3); 3.5 (m, CHS); 2.9 (m, CH_2); 1.4 (m, CH_3); 1.3 (s, CH_3). ^{13}C NMR: δ = 15.7 (Me, J_{CP} = 8.4); 63.7 (CH_2O, J_{CP} = 6.0); 44.9 (SCH); 36.5 (CH_2, J_{CP} = 5.0); 42.5 ($\underline{C}(CH_3)_3$); 30.8 ($C(\underline{C}H_3)_3$; 21.3 (CH_3, J_{CP} = 7.0). ^{31}P NMR: δ = 93.1. Yield = 88%.

Compound **4a**: ^{1}H NMR: δ = 4.2 (m, CH_2O); 4.6 (m, CH_2O); 5.3 (m, CH_2=); 5.9 (m, CH=); 1.3 (t, CH_3). ^{13}C NMR: δ = 16.0 (Me, J_{CP} = 7.0); 64.2 (CH_2O, J_{CP} = 5.4); 68.1 (CH_2O, J_{CP} = 5.3); 133.3 (CH=, J_{CP} = 6.2); 118.5 (CH_2=, J_{CP} = 6.8). ^{31}P NMR: δ = 70.4.

Calcd: C 40.00; H 7.14; O 22.86; P 14.76; S 15.24.
Found: C 40.12; H 7.25; O 22.59; P 14.21; S 15.32.

Compound **4b**: ^{1}H NMR: δ = 4.2 (m, CH_2O); 3.5 (dd, CH_2S); 5.3 (m, CH_2=); 5.9 (m, CH=); 1.3 (t, CH_3). ^{13}C NMR: δ = 15.8 (Me, J_{CP} = 8.2); 63.9 (CH_2O, J_{CP} = 5.5); 36.2 (CH_2S); 132.3 (CH=, J_{CP} = 6.2); 118.3 (CH_2=, J_{CP} = 6.9). ^{31}P NMR: δ = 95.0.

Compound **4c**: ^{1}H NMR: δ = 4.2 (m, CH_2O); 4.6 (m, CH_2O); 5.3 (m, CH_2=); 5.9 (m, CH=); 2.0 (m, CH_2); 1.3 (s, CH_3); 2.6 (m, CH_2S). ^{31}P NMR: δ = 70.6.

Compound **4d**: ^{1}H NMR: δ = 4.2 (m, CH_2O); 3.5 (m, CH_2S); 5.3 (m, CH_2=); 5.9 (m, CH=); 2.0 (m, CH_2); 1.3 (s, CH_3); 2.6 (m, CH_2S). ^{31}P NMR: δ = 95.7.

Compound **5a**: ^{1}H NMR: δ = 4.2 (m, CH_2O); 1.3 (m, Me); 3.3 (m, CHS); 1.6 (m, CH_2); 1.3–1.5 (m, CH_2); 0.9 (t, CH_3). ^{13}C NMR: δ = 15.6 (Me, J_{CP} = 8.5); 63.4 (CH_2O, J_{CP} = 5.5); 45.4 (CHS, J_{CP} = 3.7); 37.8 (CH_2, J_{CP} = 7.5); 26.5 (CH_2); 28.7 (CH_2); 32.5 (CH_2); 22.3 (CH_2); 22.8 (Me, J_{CP} = 4.2); 13.7 (Me). ^{31}P NMR: δ = 95.9. Yield = 67%.

Calcd: C 48.33; H 9.06; S 21.47; O 10.73; P 10.40.
Found: C 48.41; H 9.12; S 21.32; O 10.80; P 10.01.

Compound **5b**: ^{31}P NMR: δ = 96.4. Yield = 33%.

Compound **5c**: ^{1}H NMR: δ = 4.2 (m, CH_2O); 1.3 (s, Me); 2.6 (m, CH_2S); 2.0 (m, CH_2); 3.4 (m, CHS); 1.4–1.7 (m, CH_2); 1.5 (d, CH_3); 0.9 (t, Me). ^{31}P NMR: δ = 95.5. Yield = 90%.

Compound **5d**: ^{31}P NMR: δ 95.9. Yield = 10%.

Compound **6a**: ^{1}H NMR: δ = 4.1 (m, CH_2O); 1.3 (t, CH_3); 2.8 (m, CHS); 3.0 (m, CH_2S); 1.5 (d, CH_3). ^{13}C NMR: δ = 15.9 (Me, J_{CP} = 8.3); 64.0 (CH_2O, J_{CP} = 7.0); 45.2 (CHS); 40.9 (CH_2); 21.3 (Me). ^{31}P NMR: δ = 94.7. Yield = 53%.

Compound **6b**: ^{1}H NMR: δ = 4.1 (m, CH_2O); 1.3 (t, CH_3); 2.8 (m, CHS); 3.0 (m, CH_2S); 1.5 (d, CH_3). ^{13}C NMR: δ = 15.9 (Me, J_{CP} = 8.3); 64.0 (CH_2O, J_{CP} = 7.0); 41.2 (CH_2S); 41.1 (CH); 21.3 (Me). ^{31}P NMR: δ = 94.6. Yield = 35%.

REFERENCES

1. A. Cameron, Proc. Inst. Mech. Eng. (I. Mech. E. Conf., 1987), p. 335.
2. J. M. Palacios, *Wear*, **111**, 41 (1987).
3. G. W. Georgi, "Motor Oil and Engine Lubrification," (Reinhold Publishing Corp., N.Y., 1950), p. 167.
4. P. Brocha and R. D. O'Brien, *Biochemistry*, **7**, 1555 (1970).
5. R. L. Metcalf, "Organic Insecticides," (Intersciences Publishers, Inc., N.Y., 1955), p. 251.
6. J. M. Ndong Mebah, J. L. Mieloszynski and D. Paquer, *Phosphorus, Sulfur and Silicon*, **78**, 215 (1993).
7. J. M. Ndong Mebah, J. L. Mieloszynski and D. Paquer, *Phosphorus, Sulfur and Silicon*, **73**, 49 (1992).
8. N. Ysenberg and M. Grdinic, *J. Chem. Educ.*, **46**, 601 (1969).
9. G. Norman, W. M. Lesuer and D. Martin, *J. Am. Chem. Soc.*, **74**, 161 (1952).