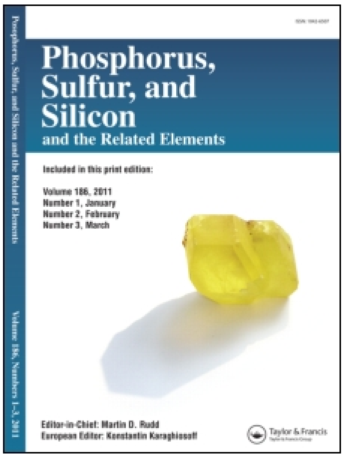

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REACTIVITY OF DITHIOPHOSPHORIC ACID TOWARDS SULFURATED MONOSUBSTITUTED ALKYNES IN PRESENCE OF TRANSITION-METAL-CATALYST

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REACTIVITY OF DITHIOPHOSPHORIC ACID TOWARDS SULFURATED MONOSUBSTITUTED ALKYNES IN PRESENCE OF TRANSITION-METAL-CATALYST

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The reactivity of sulfurated monosubstituted alkynes with dithiophosphoric acid (noted Z-H) has been investigated. Depending on the transition-metal-catalyst (Ni, Pd, Rh) and solvent (benzene or THF), two types of alkenes can be isolated: $Z\text{-}CH{=}CH\text{-}CH_2\text{-}SR$ and/or $Z\text{-}C(CH_2\text{-}SR){=}CH_2$. The selectivity of this reaction was studied. ^{13}C and ^{31}P NMR of these new sulfurated alkenes are reported.

Keywords: Dithiophosphoric acid; alkynes; sulfurated alkenes; ^{13}C NMR; ^{31}P NMR

INTRODUCTION

We have previously published our results of the addition of dithiophosphoric acid (DTPA, noted Z-H) on monosubstituted sulfurated alkynes[1]. We have shown that the addition of Z-H on sulfurated alkynes could lead to regioselective reaction, depending on reagents (radical reaction (AIBN) or ionic reaction (MeCN or Triton B)).

In this present work, we studied the influence of transition-metal-catalyst (Pd, Rh, Ni) on the same reaction. We report our results concerning the reactivity of diisopropyldithiophosphoric acid with a monosubstituted sulfurated alkyne. The selected alkyne have a sulfur which is not directly bound on the triple bond.

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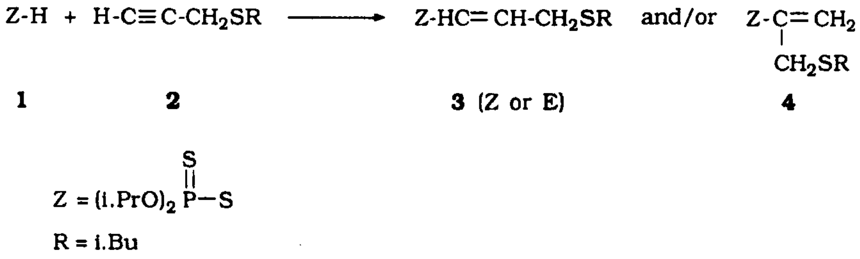
RESULTS

Two types of alkenes can be isolated:



$$\underset{\mathbf{1}}{Z\text{-}H} + \underset{\mathbf{2}}{H\text{-}C{\equiv}C\text{-}CH_2SR} \longrightarrow \underset{\mathbf{3}\ (Z\ \text{or}\ E)}{Z\text{-}HC{=}CH\text{-}CH_2SR} \quad \text{and/or} \quad \underset{\mathbf{4}}{Z\text{-}\underset{|\atop CH_2SR}{C}{=}CH_2}$$

$$Z = (i.PrO)_2\overset{S\atop ||}{P}\text{—}S$$

$$R = i.Bu$$

The results are reported in Table I. The reaction gives always 100% of conversion. We used different catalysts: $Pd(OAc)_2$, $PdCl_2$, $(Ph_3P)_2PdCl_2$, $(Ph_3P)_2RhCl$, $(Ph_3P)_2NiCl_2$ with two solvents: benzene (Bz) or THF.

In Table I, we have reported the δ values observed in the ^{31}P NMR, and the retention time (Tr) observed in GC/MS. For all the trials, the δ values observed in the ^{31}P NMR are similar, but not the retention time. Indeed, we always used the same column of chromatography but experimental conditions could change (pressure, temperature, programmation).

We can note that alkene **4** has always a lower retention time than alkene **3**. When a compound is not identified in GC/MS, no value is written in Table I for Tr.

Note about "others" compounds:

We observed two "other" compounds:

- The first (δ = 100,3 ppm in the ^{31}P NMR) has been already identified when we worked on the sulfurated alkynes[2]. The product is not identified in GC/MS. We are not sure of its structure, but it could be derived from DTPA.
- For the second compound (δ = 75,4 ppm in the ^{31}P NMR), not identified in GC/MS, we have not totally established its structure.

DISCUSSION/CONCLUSION

Isolated compounds have been characterized by ^1H, ^{13}C, ^{31}P NMR and analyzed by GC/MS. In the ^1H NMR, only the δ values of CH= and CH_2= are different (Table II).

TABLE I Reactivity of Z-H on H-C≡C-CH_2S-i.Bu

Cat.	*Solvent*	*Alkene 3*	*Alkene 4*	*Others*	*NMR ^{31}P*	*Tr GC/MS*
$Pd(OAc)_2$	Bz	E: 5%			84,5	35,4
		Z: 9%			85,3	35,4
			86%		85,9	33,9
$Pd(OAc)_2$	THF	E: 48%			84,5	34,6
		Z: 43%			85,3	34,6
			3%		85,9	
				6%	100,3	
$PdCl_2$	Bz	E: 2%			84,5	31,4
		Z: 2%			85,4	31,4
			92%		85,9	30,3
				4%	100,3	
$PdCl_2$	THF	E: 49%			84,5	32,1
		Z: 49%			85,3	32,1
				2%	100,3	
$(Ph_3P)_2/PdCl_2$	Bz	E: 3%			84,5	31,7
		Z: 3%			85,3	31,7
			93%		85,9	30,6
$(Ph_3P)_2/PdCl_2$	THF	E: 62%			84,5	32,2
		Z: 37%			85,3	32,2
$(Ph_3P)_2$ /RhCl	Bz	E: 5%			84,5	31,5
		Z: 12%			85,4	31,5
			83%		85,9	30,3
$(Ph_3P)_2$/RhCl	THF	E: 50%			84,5	32,6
		Z: 50%			85,4	32,6
$(Ph_3P)_2/NiCl_2$	Bz	E: 6%			84,5	31,6
		Z: 10%			85,4	31,6
			83%		85,9	30,4
$(Ph_3P)_2/NiCl_2$	THF	E: 76%			84,5	31,3
		Z: 15%			85,4	31,3
			trace			29,2
				8%	75,4	

The same fact can be noticed in the ^{13}C and ^{31}P NMR spectra (Table II).

We also observed a complex system for hydrogenes of compound **3** (-CH═CH-CH_2), and a relatively simple system for compound **4** (-C═CH_2). In GC/MS, E and Z isomers of alkene **3** give one single signal.

Fragmentations observed are, on an average:

Alkene **3** (E + Z): Tr = 32,3 min; m/z = 129 (100%): $[i.Bu\text{-}S\text{-}CH_2\text{-}C_2H_2]^+$

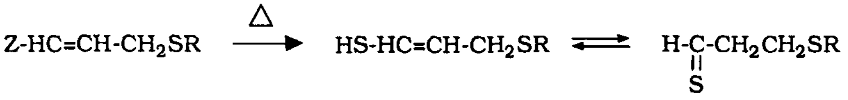
Alkene **4**: Tr = 30,6 min; m/z = 169 (100%): $[(HO)_2\text{-}P(S)\text{-}S\text{-}C_3H_4]^+$

TABLE II NMR of alkenes (δ in ppm, J in Hz)

N°	*CH=*	*CH=*	*CH$_2$=*	*Me i*-Pr	*CH i*-Pr	*CH$_2$S*	*SCH$_2$*	*CH*	*Me*
	^{1}H	^{1}H	^{1}H	^{1}H	^{1}H	^{1}H	^{1}H	^{1}H	^{1}H
3E	6,0m J = 15	5,9m J' = 8,1		1,3m	4,8m	3,2m	2,6m	1,7m	1,0m
3Z	6,2m J = 10,2	5,9m J' = 10,1		1,3m	4,8m	3,2m	2,6m	1,7m	1,0m
4			5,7m J = 4,1, J' = 1,5 5,6m J = 4,1, J" ≈ 0	1,3m	4,8m	3,4m	2,6m	1,7m	1,0m
J = J(ab); J' = J(ax); J" = J(bx): x = P; a = H near of P; b = H distant of P								m = multiplet	
	^{31}P	^{13}C	^{13}C	^{13}C	^{13}C	^{13}C	^{13}C	^{13}C	^{13}C
3E	84,5	131,0 J = 10,4	119,1 J = 5,7	23,7 23,3	73,6 J = 6,7	39,8	40,2	28,1	22,0
3Z	85,3	134,5 J = 11,1	120,1 J = 3,9	23,7 23,3	73,6 J = 6,7	39,8	40,2	28,3	21,9
4	85,9	136,2 J = 8,3	124,7 J = 8,9	23,7 23,3	73,8 J = 7,4	40,3 J = 2,9	40,4	28,1	22.0
J = J(PH)									

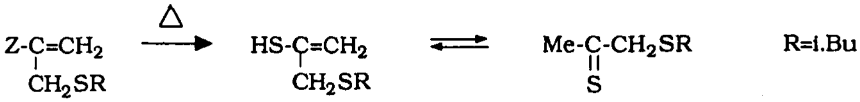
The prepared alkenes isomerize (thermic effect) to "enethiols" (thioaldehyde or thioketone). Enethiols are not present in the reaction mixture. We identified them when the injection temperature was above 200°C.

Thermic decompositions of **3** and **4** are as follows:



$$\text{Z-HC=CH-CH}_2\text{SR} \xrightarrow{\Delta} \text{HS-HC=CH-CH}_2\text{SR} \rightleftharpoons \text{H-}\underset{\underset{\text{S}}{\|}}{\text{C}}\text{-CH}_2\text{CH}_2\text{SR}$$

5



$$\text{Z-}\underset{\text{CH}_2\text{SR}}{\underset{|}{\text{C}}}\text{=CH}_2 \xrightarrow{\Delta} \text{HS-}\underset{\text{CH}_2\text{SR}}{\underset{|}{\text{C}}}\text{=CH}_2 \rightleftharpoons \text{Me-}\underset{\underset{\text{S}}{\|}}{\text{C}}\text{-CH}_2\text{SR} \qquad \text{R=i.Bu}$$

6

In GC/MS, we have:

Thioaldehyde **5**: Tr = 10,8 min; m/z = 162 ($M^{+\cdot}$); m/z = 106 (100%)

Thioketone **6**: Tr = 11,2 min; m/z = 162 ($M^{+\cdot}$); m/z = 106 (100%)

Compound **6** has been synthetized[3]: Tr and mass spectra were totally identical.

The influence of solvent is fundamental: the regioselectivity is totally reversed with the same catalyst. Benzene widely favours formation of alkene **4** with a good selectivity.

The regioselectivity is more important with THF (compound **4** is rarely present; in the opposite, with benzene, compound **3** is present up to 17%). This difference could be due to the possible liaison of the atom of oxygen (of THF) with the metal of different catalysts.

To isolate alkene **3**, we can use all the catalysts, but for alkene **4** we would prefer $PdCl_2$ or $(Ph_3P)_2PdCl_2$.

EXPERIMENTAL

^{13}C NMR and ^{1}H NMR spectra were recorded on a BRUKER AC 250 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard.

^{31}P NMR spectra were recorded on a BRUKER AC 250 spectrometer in $CDCl_3$ using H_3PO_4 as external standard.

The chemical shifts (ppm) are presented in Table II (abbreviations: m (multiplet)).

Mass spectra were realized after GC/MS coupling on HP display (capillary columm SE30, 25 meters; temperature programmation: 60°C during 3 minutes, then 4°C/min until 300°C). The results are summarized in Table I.

General Procedure

To a solution of benzene or THF (30 ml) and catalyst (0,02 equivalent) is added alkyne (15 mmol). 15 mmol of dithiophosphoric acid is added dropwise under N_2 atmosphere.

The mixture is heated at reflux for 16 hours and the precipitated metal complex is removed through celite.

The resultant mixture is washed with a solution of sodium hydroxide, and the organic layer is dried with sodium sulfate. The solvent is removed under reduced pressure.

Products are isolated by chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (90/10) as eluent.

References

[1] V. Dodin-Carnot, M. Curci, J. C. Wilhelm, J. L. Mieloszynski, D. Paquer, *Phosphorus, Sulfur, and Silicon*, **107**, 219 (1995) and cited references.

[2] V. Dodin-Carnot, B. Stephan, M. Curci, J. L. Mieloszynski, D. Paquer, *Phosphorus, Sulfur, and Silicon*, **108**, 1 (1996).

[3] We realized these synthesis in Thioorganic compounds Laboratory of M. Masson, Caen (France).