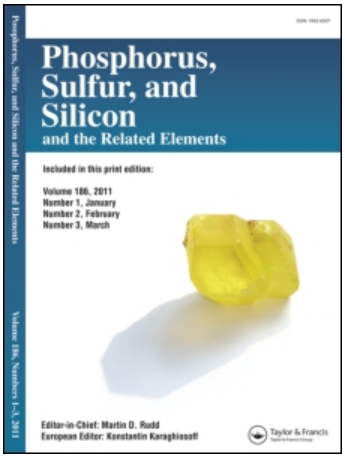


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# ACTION OF DITHIOPHOSPHORIC ACID TOWARDS SULFURATED ALKYNES IN PRESENCE OF TRANSITION-METAL-CATALYST

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# ACTION OF DITHIOPHOSPHORIC ACID TOWARDS SULFURATED ALKYNES IN PRESENCE OF TRANSITION-METAL-CATALYST

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The reactivity of sulfurated substituted alkynes with dithiophosphoric acid has been investigated. Depending on the catalyst (Pd, Rh, Ni) and the solvent (benzene or THF) two types of alkenes can be isolated: Z—C(Me)=CH—R and/or Z—C(R)=CH—Me. The selectivity of this reaction was studied. $^{13}C$ and $^{31}P$ NMR of these new sulfurated alkenes were reported.

*Key words:* Dithiophosphoric acid, alkynes, sulfurated alkenes. $^{13}C$ NMR, $^{31}P$ NMR, transition-metal-catalyst.



## INTRODUCTION

We have previously published our results of addition of dithiophosphoric acid (DTPA, noted Z—H) on substituted sulfurated alkynes[1] (Me—C≡C—SR). In this work, 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)).

We have recently completed this study with addition of the same DTPA on monosubstituted sulfurated alkynes[2] (H—C≡C—$CH_2$SR). According to the reagents, we can also obtain regioselective additions.

In this present work, we studied the influence of transition-metal-catalyst (Pd, Rh, Ni) on the same reaction. We report our preliminary results concerning the reactivity of DTPA with substituted sulfurated alkynes. The same DTPA (Z—H) and the same alkyne have been used here.

## RESULTS

Two types of alkenes can be isolated:

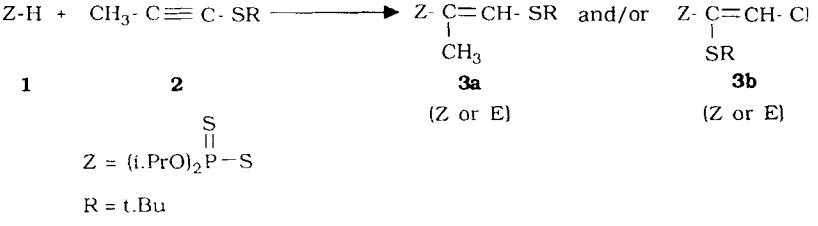


TABLE I

Reaction of Z—H on $CH_3$—C≡C—St.Bu

| Cata | Solvent | Alkene 3a | Alkene 3b | Autres | NMR $^{31}P$ | Tr GC/MS | GC/MS 100% |
|---|---|---|---|---|---|---|---|
| $Pd(OAc)_2$ | Bz | E : 58% | | | 85,2 | 29,9 | 169 |
| | | Z : 20% | | | 86,7 | 29,3 | 169 |
| | | | E : 11% | | 86,8 | 28,0 | 201 |
| | | | | 11% | 100,3 | | |
| $Pd(OAc)_2$ | THF | E : 78% | | | 85,2 | 29,9 | 169 |
| | | Z : 14% | | | 86,7 | 29,3 | 169 |
| | | | E : 5% | | 86,8 | 28,0 | 201 |
| | | | | 3% | 100,3 | | |
| $PdCl_2$ | Bz | E : 33% | | | 85,2 | 29,1 | 169 |
| | | Z : 2% | | | 86,7 | | |
| | | | E : 62% | | 86,8 | 27,4 | 201 |
| | | | | 3% | 100,4 | | |
| $PdCl_2$ | THF | E : 82% | | | 85,2 | 29,6 | 169 |
| | | Z : 14% | | | 86,7 | | |
| | | | E : 4% | | 86,8 | | |
| $(Ph_3P)_2$ | Bz | E : 17% | | | 85,2 | 29,5 | 169 |
| $/PdCl_2$ | | Z : 5% | | | 86,7 | | |
| | | | E : 78% | | 86,8 | 28,0 | 201 |
| $(Ph_3P)_2$ | THF | E : 82% | | | 85,2 | 29,2 | 169 |
| $/PdCl_2$ | | Z : 15% | | | 86,7 | | |
| | | | E : 3% | | 86,8 | 26,7 | 201 |
| $(Ph_3P)_2$ | Bz | | E : 100% | | 86,8 | 28,6 | 201 |
| /RhCl | | | | | | | |
| $(Ph_3P)_2$ | THF | E : 86% | | | 85,2 | 29,9 | 169 |
| /RhCl | | Z : 4% | | | 86,7 | | |
| | | | E : 10% | | 86,8 | 27,1 | 201 |
| $(Ph_3P)_2$ | Bz | | E : 100% | | 86,8 | 28,3 | 201 |
| $/NiCl_2$ | | | | | | | |
| $(Ph_3P)_2$ | THF | E : 49% | | | 85,2 | 29,5 | 169 |
| $/NiCl_2$ | | Z : 2% | | | 86,7 | | |
| | | | E : 49% | | 86,8 | 27,7 | 201 |

The results are reported in Table I. The conversion rate in comparison with alkyne is always 100%.

We used different catalysts: $Pd(OAc)_2$), $PdCl_2$, $(Ph_3P)_2PdCl_2$, $(Ph_3P)_2RhCl$, $(Ph_3P)_2NiCl_2$. The influence of solvent, benzene (Bz) or THF, is also fundamental.

In Table I, we have reported the $\delta$ values observed in the $^{31}P$ NMR, retention time (Tr) observed in GC/MS and the value of the 100% signal in GC/MS.

For all the trials, the $\delta$ 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 **3b** has always a Tr lower than alkene **3a**. When a compound is not identified in GC/MS, no value is written in Table I for Tr and GC/MS.

TABLE II

NMR of alkenes ($\delta$ in ppm, $J$ in Hz)

| | i.Pr Me | i.Pr CH | CH= | C= | Me | Me t.Bu | C t.Bu |
|---|---|---|---|---|---|---|---|
| | $^1H$ | $^1H$ | $^1H$ | | $^1H$ | $^1H$ | $^{31}P$ |
| **3a (E)** | 1,35m | 4,85m | 6,4m J(PH)=3,5 | | 2,2m J(PH)=2,1 | 1,4s | 85,2 |
| **3a (Z)** | 1,35m | 4,85m | 6,6m J(PH)=4,5 | | 2,0m J(PH)=2,6 | 1,4s | 86,7 |
| **3b (E)** | 1,35m | 4,85m | 6,8m J(PH)=3,5 J(HH)=6,9 | | 2,0m J(HH)=6,9 | 1,4s | 86,8 |
| | $^{13}C$ | $^{13}C$ | $^{13}C$ | $^{13}C$ | $^{13}C$ | $^{13}C$ | $^{13}C$ |
| **3a (E)** | 23,6 23,3 | 73,4 | 130,0 J(PH)=11,4 | 123,3 J(PH)=8,6 | 26,2 | 30,9 | 44,0 |
| **3a (Z)** | 23,6 23,3 | 73,4 | 132,8 | 121,5 | 26,3 | 30,9 | 44,0 |
| **3b (E)** | 23,6 23,3 | 73,4 | 150,2 J(PH)=6,9 | 123,7 J(PH)=9,6 | 18,6 | 30,9 | 44,2 |

s=singulet , m=multiplet



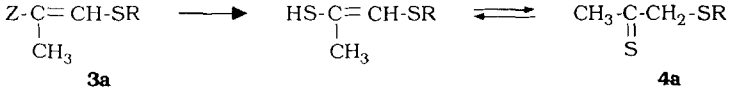
## DISCUSSION/CONCLUSION

Isolated compounds have been characterized by $^1H$, $^{13}C$, $^{31}P$ NMR and analyzed in GC/MS. We identified E and Z isomers of alkene type **a** but only E isomer for alkene type **b**.

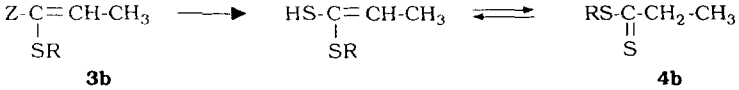
In the $^1H$ NMR, the hydrogenes of i.Pr—O and t.Bu have always the same $\delta$ value for all alkenes. The $\delta$ values of CH= and Me on the double bond are different (Table II). The same fact can be noticed in the $^{13}C$ and $^{31}P$ NMR spectra (Table II).

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

Thermic decompositions of **3a** and **3b** are as follows:




**3a** **4a**




**3b** **4b**

When alkene **3a** is preponderant, the corresponding thioketone **4a** is the major product. In the same way, we obtain the dithioester **4b** from the alkene **3b**. These products have been easily identified in GC/MS.

Like alkenes **3a** and **3b**, the mass spectra of thioketones **4a** are different from that of the dithioesters **4b**.

Fragmentations observed are, on an average:

Alkene **3a**: 342 (13%), 285 (6%), 253 (14%), 243 (7%), 201 (42%), **169** (100%), 139 (33%), 131 (5%), 106 (28%), 97 (22%), 57 (64%), 41 (51%)

Alkene **3b**: 342 (2%), 285 (21%), 243 (13%), **201** (100%), 139 (10%), 131 (12%), 106 (7%), 97 (12%), 57 (39%), 41 (30%)

Thioketone **4a**: 162 (39%), 106 (15%), 73 (48%), **57** (100%), 45 (23%), 41 (39%)

Dithioester **4b**: 162 (24%), **106** (100%), 59 (62%), 57 (63%), 45 (32%), 41 (52%)

(Distinction of isomer Z and E is difficult, only possible in GC/MS).

The 100% fragments are

m/z = 201: $[(HO)_2—P(S)—S—C(=CH—Me)—S]^+$
m/z = 169: $[(HO)_2—P(S)—S—C(Me)=CH]^+$
m/z = 106: $[HS—C(S)—CH2—Me]^+$
m/z = 57: $[t.Bu]^+$

We have synthetized compounds **4a** and **4b**[3]: Tr and mass spectra were totally identical.

We can see that when we change the solvent (Bz or THF), the regioselectivity is totally reversed with the same catalyst (except with $Pd(OAc)_2$). Benzene widely favours formation of alkene **b** with a good selectivity.

The selectivity of the E isomer is due to geometric phenomenon (crowding of Z form for alkene **a** or **b**).

To explain the regioselectivity, we have to refer to asymmetric synthesis realized with catalysts[4]: the structure of the employed catalyst involves generally one possible position of reagent in the space. In our case, we think that the metal (of catalyst)/ oxygen (of THF) interactions widely favour formation of alkene **a**.

*Note* about "Other" compounds: The characterized compound is always the same with a $\delta$ value in the $^{31}P$ NMR at 100.3 ppm. Unfortunately we could not identify these compounds in the GC/MS, and the obtained percentage is too weak to isolate chemically these products.

## EXPERIMENTAL

$^{13}C$ NMR and $^1H$ 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: s (singulet), m (multiplet)).

Mass spectra were realized after GC/MS spectra on HP display (capillary column 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.

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2. V. Dodin-Carnot, M. Curci, J. C. Wilhelm, J. L. Mieloszynski and D. Paquer, to be published.
3. We realized these synthesis in Thioorganic compounds Laboratory of M. Masson. Caen, France.
4. (a) W. R. Roush, *J. Org. Chem.*, **56,** 4151 (1991) and cited references; (b) W. Oppolzer, *Pure and Appl. Chem.*, **60,** 39 (1988) and cited references.