



OLEFINS FOLLOWED BY THE ^1H NMR MARKER, OF α -MERCURY CARBONYLS USING WITTIG REACTION.

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ABSTRACT

This study is an extension of the Wittig reaction on the synthesis of mercuric olefins from α -mercuric carbonyls which are known as thermodynamically and kinetically instable compounds.

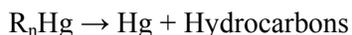
The Wittig reaction with appropriate alkylidens phosphoranes give mercuric olefins with pronounced stereospecificity (E) in a good yield.

Herein the identification of acquired thiocyanomercuri-4-ene-2 (methyl-2-ene 2) alkyl butenoate is being established by ^1H -NMR spectroscopic methods of actif ^{199}Hg .

Key words: Organomercuric compounds, $^1\text{HNMR}$, Hg marker, stereochemistry.

INTRODUCTION

Organomercuric constitute are used in a wide range of investigation, especially in pesticides, preservatives etc; and as intermediate agent to obtain butenolids¹, which exist in nature and are of important biological activities². For these reasons the chemistry of organomercury have a privileged place in organometallic synthesis strategy. However, the synthesis of organomercuric is quiet delicate, because of the lability of the carbon-mercury bond as shown in the diagram of bonds dissociation, Schem-1^{2,3} the average energy of the bonds, $\bar{D}(\text{M}-\text{CH}_3)$ in $\text{M}(\text{CH}_3)_n$ decompose often the exempted products till until the appearance of metal.



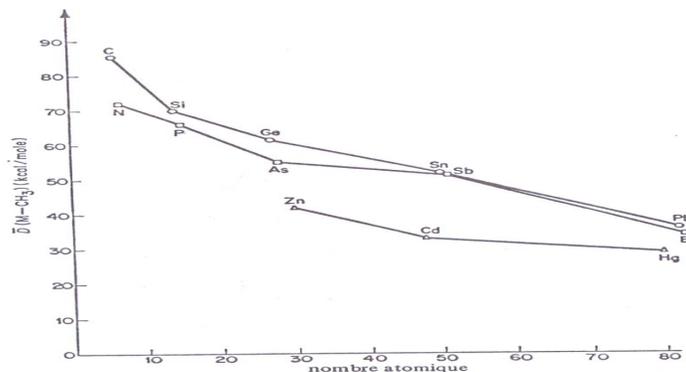
In this fact, monitoring of the organomercuric synthesis with $^1\text{HNMR}$ of ^{199}Hg actif labelled seems to be useful to determine the Hg-C bond. Due to the usefulness of organomercuric compounds, we have taken synthesis of acetomercuri-2-diacetoxy-1-ethane in basic aqueous⁴. The thiocyanation of the latter affords the thiocyanomercury acetaldehyde, which reacts with Alkylidens phosphoranes^{5,6} to give Mercuric olefins: (E) thiocyanomercuri-4 en-2 (methyl-2 en 2) Alkyl butenoate.

EXPERIMENTAL

Work conditions:

Synthesis of organomercuric compounds is realised at adequate temperature and absence of reducing agents Hg^{2+} cation. Solvents were distilled and dried under nitrogen, before use in

reaction. All the reactions were monitored by $^1\text{H-NMR}$ and analytical TLC plates hexane/chloroform/ethyl acetate (3: 1: 2).



Scheme-1: Diagram of some averaged energies bonds dissociation $\bar{D}(\text{M-CH}_3)$ in $\text{M}(\text{CH}_3)_n$.

Preparation of phosphoranes Alkylidens, Wittig reagents¹⁷⁻²⁰

We have used a range of three of Wittig reagents in the synthesis of product **i** ($i = 1-3$):
 Carboethoxyethyliden of triphenylphosphorane (**4**) with $\text{R}' = \text{CH}_3$, $\text{R}'' = \text{COOCH}_2\text{CH}_3$ ^{19,20}.
 Carboethoxyethyliden of triphenylphosphorane (**4**) with $\text{R}' = \text{H}$, $\text{R}'' = \text{COOCH}_3$ ¹⁸.
 Carboethoxyethyliden of triphenylphosphorane (**4**) with $\text{R}' = \text{H}$, $\text{R}'' = \text{COOCH}_2\text{CH}_3$ ²¹.

Example of carbethoxyethyliden triphenylphosphorane^{19,20} which can be prepared in two steps:

Step1:

300ml a solution of 131g of triphenylphosphine (0,5mol) and 108 g ethyl bromide in 300ml of dried toluene is refluxed for (48- 60 hours), until precipitation of ethyl bromide triphenyl phosphonium ($F=207-208\text{ }^\circ\text{C}$), this precipitate is washed with toluene and well dried to be used in the 2nd stage.

Step2:

A solution ethyl bromide triphenyl phosphonium 37.3mg (0.1mol) in 400 ml of toluene is refluxed for 15min, to 40 ml of the solvent is evaporated then we add about 12.2g (0.1mol) of *t*-ButOH under nitrogen atmosphere and the mixture is put back to reflux for 30 min, and then cooled down .At room temperature a solution of 5.43 g of ethyl chloroformate (0.05mol) in 10 ml of toluene was added to the mixture reaction. Then put to reflux for 40min. the mixture is cooled down and filtered, then evaporation of solvent to obtain the alkylidenephosphorane as solid recrystallised from ethyl acetate ($F=300\text{ }^\circ\text{C}$).

Spectroscopic analysis:

The infrared spectra of all products were performed on a spectrophotometer by KBr brand PERKIN Elmer 177. $^1\text{HNMR}$ spectra were recorded in D_2O , $(\text{CD}_3)_2\text{CO}$ and CDCl_3 [TMS] by a spectrophotometer type 80 Bruker Wp Sy and type Avenca Bruker DPX 250.

Melting points of the synthesized products were taking by the aid of an ordinary Banc Kofler apparatus.

Synthesis of products:

Synthesis of acetomercuri-2-diacetoxy-1-ethane (**1**):

To a mixture of about 0.86 g vinyl acetate (0.01mol) and 3 ml of pure acetic acid was added to 3.12 g of mercuric ethyl (0.01mol).the mixture was heated up to $60\text{ }^\circ\text{C}$ until the total dissolution of mercuric

acetate, then cooled down, 20 ml of petroleum ether were added to the mixture after 10 sec compound (1) was precipitate as white crystal.

Synthesis of thiocyanomercuri-acetaldehyde (3):

3.20g of product (1) (0.01mol) was dissolved in 50ml of distilled water, we added about 0.4 g of NaOH (0.01mol) and left stirred at 30 °C. A solution of 0.76 g of ammonium thiocyanate (0.01mol) in 10ml of distilled water was added drop wise to the mixture; then after was left to stir for about 1hour time. A solid precipitated as white crystal product (3). (In a yield of 82%, F=135 °C)

Synthesis of olefins Mercury (1, 2, 3):

Synthesis of the three products: Ethyl thiocyanomercuri 4-ene – 2-methyl – 2-butenate (1), Ethyl thiocyanomercuri-4ene-2-butenate (2), and Thiocyanomercuri-4ene-2-butenate of methyl (3) were obtained by a common experimental procedure.

In around flash 100 ml, we introduce under nitrogen about 3g (0.01mol) of Thiocyanomercuriacetaldehyde (3). About 0.01mol of Wittig reagent and 50ml of distilled and dried toluene was added. The mixture was heated up to 80 °C with stirring until a total disappearance of the solid phase. Then the reaction mixture was cooled and filter to remove toluene evaporated under vacuum. The residu was washed through by of it's triphenylphosphine oxide by ethanol. The solid remaining (olefin) is recrystallized in ethanol.

Characterization of products obtained:

Acetomercuri-2 diacetoxy-1Ethane (1)

$C(H_3^a)COOHgC(H_2^b)C(H_1^c)(OOC(H_3^d))_2$

White Crystal

Yield: 92%

Melting Point: 135°C

$\delta_{ppm}^1HNMR (D_2O/TMS 250MHz)$: 2,04 (s, 3H^a); 2,08 (s, 6H^b); 2,24 (dd, $J_{HgH}=273,8 Hz$, $J_{cb} = 4,48 Hz$, 2H^b); 7 (t, $J_{bc} = 4,48 Hz$, 1H^c).

IR (KBr) $\nu=3000 cm^{-1}$ (CH₃); $\nu=1760 cm^{-1}$ (C=O)

Thiocyanomercuriacetaldehyde (3) :

$NCSHgC(H_2^a)C(H_3^b)O$

White Crystal

Yield: > 90%

Melting Point: 82°C

$\delta_{ppm}^1HNMR ((CD_3)CO /TMS 250MHz)$: 2,88 (dd, $J_{ab} = 4,75 Hz$, $J_{Hg-H} = 296 Hz$, 2H^a); 9,54 (t, $J_{ab} = 7,8 Hz$; H^b).

IR (KBr) $\nu=2100 cm^{-1}$ (SCN); $\nu=1650 cm^{-1}$ (C=O).

Thiocyanomercuri-4ene-2methyl-2butenoate d'ethyl (E) (1) :

$NCSHgC(H_2^a)C(H^b)=CC(H_3^c)COOC(H_2^d)C(H_3^e)$

Yield: 86%

Melting Point: 95°C

$\delta_{ppm}^1HNMR (CDCl_3 /TMS 80MHz)$: 2,88 (dd, $J_{ba} = 9,44Hz$, $J_{Hg-H} = 276 Hz$, 2H^a); 7,14 (t, $J_{ab} = 9,44 Hz$, H^b), 1,95 (s, 3H^c); 4,75 (q, $J_{ed} = 7 Hz$, 2H^d); 1,30(t, $J_{de}=7Hz$, 3H^e).

IR (KBr) $\nu = 1680 cm^{-1}$ (C=O), $\nu = 2100 cm^{-1}$ (SCN); $\nu = 1630 cm^{-1}$ (C=C).

Thiocyanomercuri-4ene-2butenoate d'ethyl (E) (2) :

$NCSHgC(H_2^a)C(H^b)=C(H^c)COOC(H_3^d)$

Yield: 81%

Melting Point: 136°C

$\delta_{\text{ppm}}^1\text{HNMR}$ ((CD₃)CO /TMS 80MHz): 2,88 (*dd*, $J_{\text{ba}} = 10$ Hz, $J_{\text{Hg-H}} = 308$ Hz, 2H^a); 3,60 (*s*, H^b); 5,05 (*d*, $J_{\text{bc}} = 15,2$ Hz, H^c); 7,14 (*q*, 3H^d),
IR (KBr) $\nu = 1680$ cm⁻¹ (C=O), $\nu = 2100$ cm⁻¹ (SCN); $\nu = 1630$ cm⁻¹ (C=C).

Thiocyanomercuri-4ene-2butenoate de methyl (E) (**3**) :

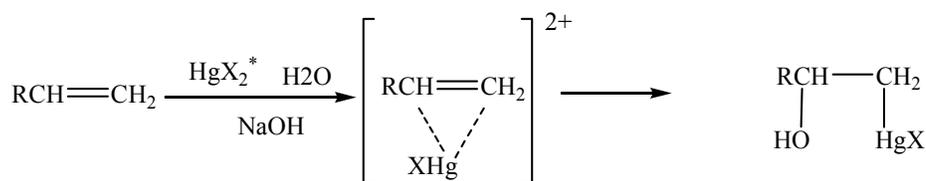
NCSHgC(H₂^a)C(H^b)=C(H^c)COOC(H₂^d)C(H₃^e)

$\delta_{\text{ppm}}^1\text{HNMR}$ ((CD₃)CO/TMS 80MHz): 1,22 (*t*, $J_{\text{de}} = 7,4$ Hz, 3H^e); 2,72 (*dd*, $J_{\text{ba}} = 9,0$ Hz, $J_{\text{Hg-H}} = 308,6$ Hz, 2H^a); 4,75 (*q*, $J_{\text{de}} = 7$ Hz, 2H^d), 5,85 (*d*, $J_{\text{bc}} = 15$ Hz, H^c); 7,12 (*q*, H^b).

IR (KBr) $\nu = 1680$ cm⁻¹ (C=O), $\nu = 2100$ cm⁻¹ (SCN); $\nu = 1630$ cm⁻¹ (C=C).

RESULTS AND DISCUSSION

In 1900, Hoffmann and Sand elaborated a pathway of synthesing the mercuration of olefins by the use of mercuric salts^{4,7-9}.

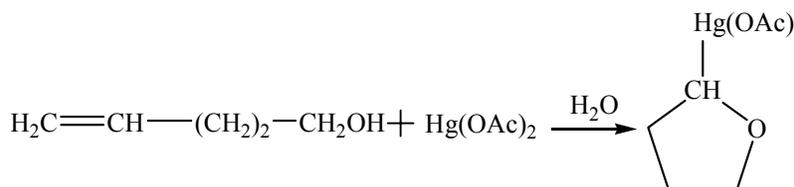


R: Alkyl

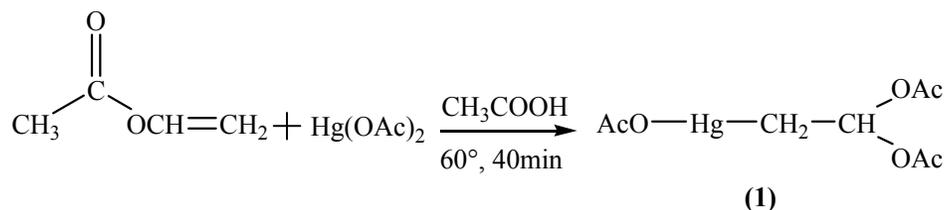
*Hg(OOCH₃)₂, Hg(NO₃)₂; HgSO₄

When the reaction is taken in alcohols we obtained the appropriate alcoholic compounds. A *Trans* addition can be produced, where as in the case of long systems, we obtain a *Cis* addition.

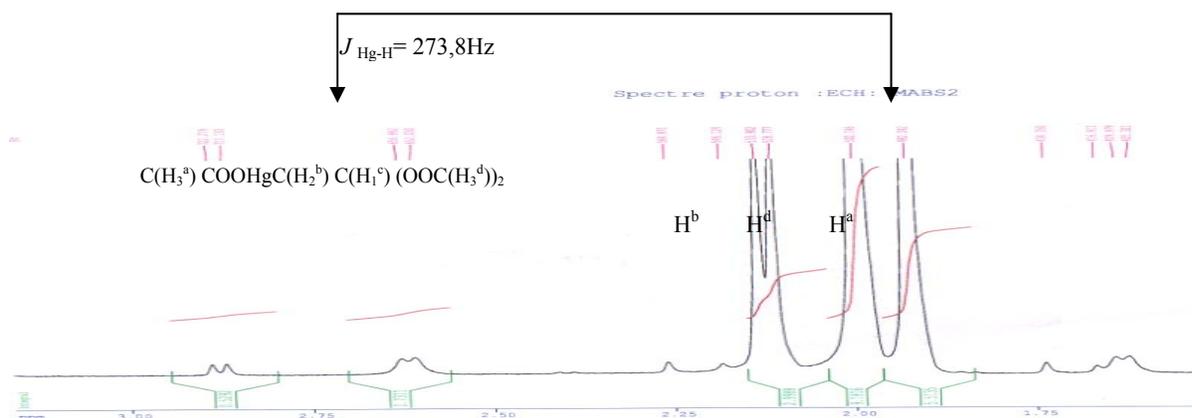
By the same way divers structures of mercuric olefins may also be made^{10,11}.



We have procreated this method to synthesize acetomercuri-2-diacetoxy-1-ethane (**1**) by a mercuration in acetic acid (solvent, reagent) of vinyl acetate be the mercuric acetate:

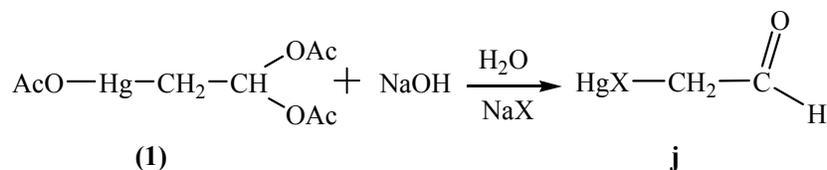


The evidence of the formation of the Hg-C bond in the product (**1**) is been established by the ¹H-NMR spectrum in scheme 2.



Scheme-2: ^1H NMR spectrum of the product (**1**).

Compound (**1**) has been treated with a basic aqueous solution (NaOH) followed by a nucleophilic substitution of NaX led to a precipitates of corresponding α -Mercuric aldehydes:

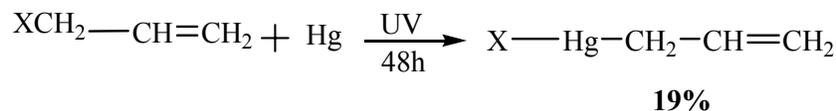


X: Cl, Br, I, SCN

This precipitate are dissolved as complexes salts by the $\text{Na}_2[\text{Hg}(\text{X})_3\text{C}_2\text{H}_3\text{O}]$ using an excess of NaX. The stability of acetoxymercuri -2-diacetoxy-1-ethane in its synthesis solvent and its substitutable of its acetoxy groups constitute a source of various α -Mercuric aldehydes. If $\text{X}=\text{SCN}$, compound (**j**) represents the thiocyno-mercuriacetaldehyd (**2**) obtained in a yield of 92%. This compound makes our starting to synthesis the mercuric olefins by the Wittig reaction.

Known various methods to accede to mercuric olefins are quiet delicate^{12,13}, However, we state in these methods. Only the mercuration of olefined products but not olefination of mercuric products as indicated in the presented work.

Radical Addition (metal, allyl halogen)

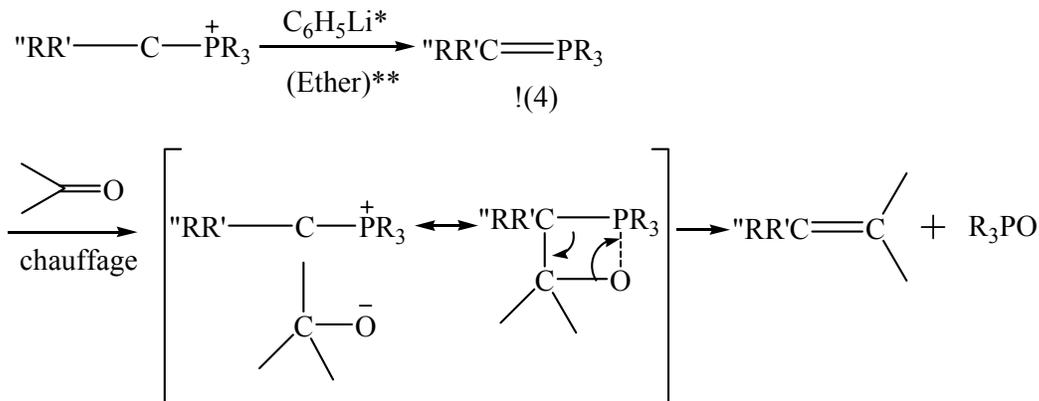


X: Cl, Br, I

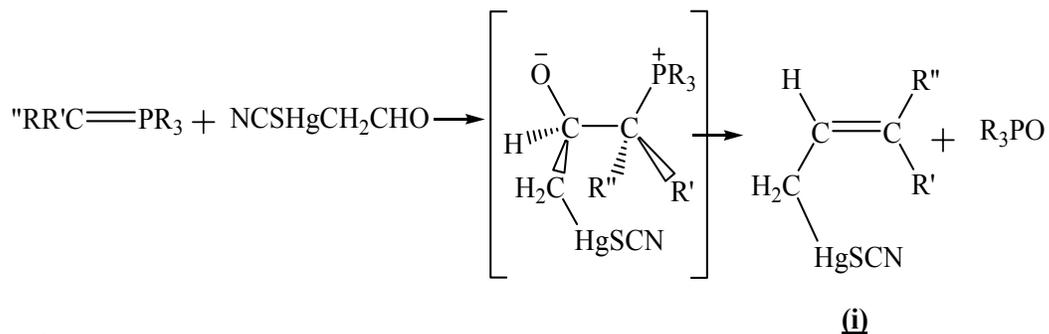
Addition of mercury salts to triple bonds



The Wittig method allows the synthesis of olefins from carbonylated compounds and alkylidens phosphoranes issued of the dehydrogenation of the quaternary phosphonium salts by bases action¹⁴⁻¹⁷.



In this case, Wittig method presents the olefins formation advantages with C=C bond. In well defined position under wild conditions. We use this method to olefined the thiomercuriacetaldehyde (**2**) by stable alkylidens phosphoranes¹⁸⁻²¹ in the aim to strength the stability the product and to stereospecifier the mechanism tow *E-threo* form^{22,23}.



- R: C₆H₅
 1: R': CH₃; R'': COOC₂H₅
 2: R': H; R'': COOC₂H₅
 3: R:H; R'': COOCH₃

Mercuric olefins are solids obtained in a yield over 80%. They have a relativity important stability by the delocalization of π bonds of C=C, C=O and the *threo* form imposed by the used stable y lure. To confirm the passages from (3) and (4) to products **i** (i = 1-3), we have used the coupling constant ($J_{\text{Hg-CH}}$)_i in ¹H-NMR spectra. Which indicate both main time presence of mercury and the conservation of Hg-C bond and the use of infrared spectra which revel the major functional groups. A complementary ¹H-NMR of structures confirmation is also used in (Table-1).

Table-1: coupling constant $J_{\text{Hg-CH}}$, melting point, IR band major products (3), **(i)** (i = 1 to 3).

| Compounds | $J_{\text{Hg-CH}}$ (Hz) | $\nu_{\text{C=O}}$ (cm ⁻¹) | $\nu_{\text{SC=O}}$ (cm ⁻¹) | $\nu_{\text{C=C}}$ (cm ⁻¹) | F (C°) | R (%) |
|-----------|-------------------------|--|---|--|--------|-------|
| (1) | 273.8 | 1760 | / | / | 82 | 92 |
| (2) | 296 | 1650 | 2100 | / | 135 | >90 |
| (3) | 296 | 1650 | 2100 | X | 135 | 92 |

| | | | | | | |
|-----|-------|------|------|------|-----|----|
| (1) | 276 | 1680 | 2100 | 1630 | 95 | 86 |
| (2) | 308 | / | / | / | 130 | 81 |
| (3) | 308.6 | / | / | / | 140 | 85 |

CONCLUSION

The redox couple Hg/Hg²⁺ has an important redox potential relatively considerable in the redox potential scale. In this case the mercurium give them to chemical compounds in which exists a particular and important active ability. We notably give as example the use of organomercuric compounds in chemotherapy, as preservation, as insecticides and intermediates agents to synthesis other products... that were roughly impossible to be obtained. Our investigation in this field has led us to contribute modestly in the synthesis of such compounds since the obtained compounds been active sites them selves.

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