



SYNTHESIS OF ETHED ORGANOMERCURIC DERIVATIVES VIA OFFMAN AND SAND REACTION

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ABSTRACT

This study is based on the synthesis of acetomeric -3-alkoxy-2-methyl butane and its derivatives. In this context the Offman and Sand reaction is been expanded by an addition of a nonionic mercuric acetate over an alkenes. This reaction gave the obtained compounds in a good yield. Structures identification is been proved by different modern spectroscopic methods such as ¹HNMR, IR, and Mass spectra, as well as analytical reactions (Nessler solution).

Keywords: Organomeric compounds, nonionic addition and Nessler solution.

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INTRODUCTION

Organomercurics were of important use in humans' life.¹ since they were used as pesticides, fungicides, preservatives and other uses. However, and because of their toxicity side their use have been limited. Now a days they are efficiently used as intermediate^{2,3} agents of biologically active organic compounds synthesis.⁴ Organomeric compounds are often kinetically and thermodynamically instable⁵; which requires adequate conditions especially for the reducing agents Hg⁺² and the heat sources in the process.

Synthesis of acetomeric 3- methyl-2-butane was carried out via Hoffman and Sand^{6,7} reactions by the addition of mercuric acetate on methyl-2- butane-2 in dry methanol. Under the same conditions using dry ethanol to obtain acetomeric- 3-ethoxy -2 methyl-2 butane. And they obtained compounds were subjected to a nucleophilic substitution reaction with NaX (X- Br,SCN) to obtain the bromo(thiocyano) 3-mercuri-methyle-2 alkoxy-2-butane.

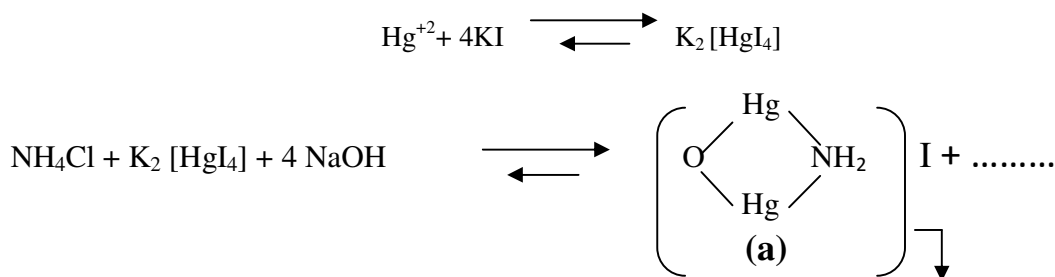
EXPERIMENTAL

Work conditions

Synthesis of organomeric compounds is realized in adequate temperature and absence of reducing agent Hg²⁺ cation. Solvents were distilled and dried under nitrogen before use. All reactions were followed by analytical TLC plates (Hexane / chloroform / ethyl acetate) (2-1-2).

Preparation of Nessler solution

Nessler solution is a mixture of Hg²⁺, KI, NH₄Cl and NaOH which gives a brown-red precipitate of iodure oxydimercuriammonium (a), Scheme-1.



Scheme-1

Chemical analysis

The Hg^{2+} cation in all obtained products was identified by the coloration of Nessler solution as red brown color.

Spectroscopic Analysis

The infrared spectra of all obtained products were performed in KBr disc Perkin 177. ^1H NMR spectra were recorded in $(\text{CD}_3)_2\text{CO}$, CD_3Cl and D_2O [TMS] by a spectra photometer type 80 Bruker WP SY and type Bruker Dpx-20. Melting Points of the synthesized products were taken by an ordinary Banc Koffler apparatus.

Synthesis of Products:

Synthesis of acetomercuri-3-methoxy-2-methyl-2-butane, i (1)

To a mixture of about 3.18 g of mercuriacetate (0.01 mol) and 0.40 g of pure methanol (0.015 mol) was added 0.7 g of methyl-2-butane-2 (0.01 mol) with stirring at room temperature until the solution became clear and then 200 ml of petroleum ether was added to the precedent solution and the mixture was left standing for 20 min at room temperature and the product (1) was precipitated as white crystals.

Synthesis of acetomercuri-3-ethoxy-2-methyl-2-butane, i (2)

Following the precedent procedure using 0.73 g of pure ethanol (0.015 mol) instead methanol.

Synthesis of mercuric derivatives products, j (1-4):

Synthesis of bromomercuri-3-methoxy-2-methyl-2-butane, j(1)

To a mixture of about 2.60 g product (1) (0.01 mol) and 0.40 g of pure methanol (0.015 mol) was added 1.03 g of NaBr (0.01 mol) in 10 cc of water. To give a precipitate which crystallized from methanol or ethanol as white crystals identified for product (1).

Synthesis of thiocyanomercuri-3-methoxy-2-methyl-2-butane, j(2)

Following the same preparation as product (1) using 0.61 g of NaSCN (0.01 mol) we obtained product (2).

Synthesis of Bromomercuri-3-ethoxy-2-methyl-2-butane, j(3)

To a mixture of about 2.74 g of product (2) (0.01 mol) and 0.73 g of pure ethanol (0.015 mol) was added 1.03 g of NaBr (0.01 mol) dissolved in 10 cc of water and the mixture was left standing at room temperature for 10 min we obtained product 3 which crystallized from ethanol as white crystals.

Synthesis of thiocyanomercuri-3-ethoxy-2-methyl-2-butane, j(4)

Following the same preparation as product (3) using 0.61 of NaSCN (0.01 mol) we obtained product (4).

Characterization of products:

Acetomercuri-3-methoxy-2-methyl-2-butane, i(1)

$\text{C}(\text{H}_3^a)\text{COOHgC}(\text{H}^b)(\text{C}(\text{H}_3^c))\text{C}(\text{OC}(\text{H}_3^d))(\text{C}(\text{H}_3^e))_2$

White crystals Mp: 35°C in a yield of: 80%

^1H NMR (CDCl_3/TMS 80 MHz): 2.04 ppm (s, 3H^a); 2.76 ppm (q, $J_{cb}=7.5$ Hz, H^b); 1.48 ppm (d, $J_{bc}=7.5$ Hz, 3H^c); 3.17 ppm (s, 3H^d); 1.23 ppm (s, 6H^e).

IR (KBr) $\nu = 1200\text{ cm}^{-1}$ (C-O-C); $\nu = 1670\text{ cm}^{-1}$ (C=O).

MS: $[\text{M}]^+$ (m/z). $\text{CH}_3\text{CO}^+ = 43$; $\text{CH}_3\text{COOHg}^+ = 260$; $\text{Hg}^+ = 20$

Acetomercuri-3 ethoxy-2 methyl-2 butane, i(2).

$\text{C}(\text{H}_3^a)\text{COOHgC}(\text{H}^b)(\text{C}(\text{H}_3^c))\text{C}(\text{OC}(\text{H}_2^d))(\text{C}(\text{H}_3^e))(\text{C}(\text{H}_3^f))_2$.

White crystals Mp 38 °C in a yield of 72%

δ_{ppm} ^1H NMR (CDCl_3/TMS 80 MHz): 2,04 ppm (*s*, 3H^a) ; 2,70 ppm (*q*, $J_{cb}=7,5$ Hz, H^b) ; 1,47 ppm (*d*, $J_{bc}=7,5$ Hz, 3H^c) ; 3,42 ppm (*q*, $J_{ed}=6,9$ Hz, 2H^d) ; 1,15 ppm (*t*, $J_{de}=6,49$ Hz, 3H^e) ; 1,24 ppm (*s*, 6H^f) .

IR (KBr) $\nu = 1200\text{ cm}^{-1}$ (C-O-C); $\nu = 1670\text{ cm}^{-1}$ (C=O).

MS: $[\text{M}]^+$ (*m/z*). $\text{CH}_3\text{CO}^+ = 43$; $\text{Hg}^+ = 202$

Bromomercuri-3 methoxy-2 methyl-2 butane, j(1).

$\text{BrHgC}(\text{H}^a)(\text{C}(\text{H}_3^b))(\text{OC}(\text{H}_3^c))(\text{C}(\text{H}_3^d))_2$

White crystals; Mp 45°C in a yield of 70%

^1H NMR (CDCl_3/TMS 80 MHz): 1 23 ppm (*s*, 6H^d); 1,48 ppm (*d*, $J_{ab}=7,5$ Hz, 3H^b); ppm at δ 2,76 ppm (*q*, $J_{ba}=7,5$ Hz, 1H^a); 3,17 ppm (*s*, 3H^c).

IR (KBr) $\nu = 1200\text{ cm}^{-1}$ (C-O-C).

MS: $[\text{M}]^+$ (*m/z*). $\text{HgBr}^+ = 281$, $\text{Hg}^+ = 202$.

Thiocyanomercuri-3 methoxy-2 methyl-2 butane, j(2).

$\text{NCSHgC}(\text{H}^a)(\text{C}(\text{H}_3^b))\text{C}(\text{OC}(\text{H}_3^c))(\text{C}(\text{H}_3^d))_2$

White crystals Mp 40 °C in a yield of 60%

^1H NMR (CDCl_3/TMS 80 MHz): 1,33 ppm (*s*, 6H^d); ppm 1,58 (*d*, $J_{ab}=7,5$ Hz, 3H^b); 2,86 ppm (*q*, $J_{bc}=7,5$ Hz, 1H^a); 3,27 ppm (*s*, 3H^c).

IR (KBr) $\nu = 1200\text{ cm}^{-1}$ (C-O-C); $\nu = 2100\text{ cm}^{-1}$ (SCN).

MS: $[\text{M}]^+$ (*m/z*). $\text{Hg}^+ = 202$, $[\text{SCN}]_2^+ = 116$, $\text{SCN}^+ = 58$

Bromomercuri-3 ethoxy-2 methyl-2 butane, j(3).

$\text{BrHgC}(\text{H}^a)(\text{C}(\text{H}_3^b))\text{C}(\text{OC}(\text{H}_2^c)\text{C}(\text{H}_3^d))(\text{C}(\text{H}_3^e))_2$

White crystals 65°C in a yield of 80%

^1H NMR (CDCl_3/TMS 80 MHz): 1, 15 ppm (*t*, $J_{cd}=6,9$ Hz 3H^d); 1,24 ppm (*s*, 6H^e); 1,47 ppm (*d*, $J_{ab}=7,5$ Hz, 3H^b); 2,75 ppm (*q*, $J_{ba}=7,5$ Hz, 1H^a); 3,42 ppm (*q*, $J_{dc}=6,9$ Hz, 2H^c) .

IR (KBr) $\nu = 1200\text{ cm}^{-1}$ (C-O-C). S.M (*m/e*). $\text{Hg}^+ = 202$, $[\text{SCN}]_2^+ = 116$, $\text{SCN}^+ = 58$

MS: $[\text{M}]^+$ (*m/z*). $\text{Hg}^+ = 202$, $\text{Br}^+ = 79,8$.

Thiocyanomercuri-3 ethoxy-2 methyl-2 butane, j(4).

$\text{NCSHgC}(\text{H}^a)(\text{C}(\text{H}_3^b))\text{C}(\text{OC}(\text{H}_2^c)\text{C}(\text{H}_3^d))(\text{C}(\text{H}_3^e))_2$

White crystals Mp 60°C in a yield of 65%

^1H NMR (CDCl_3/TMS 80 MHz): 1,25 ppm (*t*, $J_{cd}=6,8$ Hz 3H^d); 1,34 ppm (*s*, 6H^e); at δ 1,57 ppm (*d*, $J_{ab}=7,5$ Hz, 3H^b); 2,85 ppm (*q*, $J_{ba}=7,5$ Hz, 1H^a); 3,42 ppm (*q*, $J_{dc}=6,8$ Hz, 2H^c)

IR (KBr) $\nu = 1200\text{ cm}^{-1}$ (C-O-C)

MS: $[\text{M}]^+$ (*m/z*). $\text{Hg}^+ = 202$, $[\text{SCN}]_2^+ = 116$, $\text{SCN}^+ = 58$.

RESULTS AND DISCUSSION

Hoffman and Sand synthetic method used in our work is based on the addition of mercuric salts on the double bond of alkenes. Wright⁸⁻¹⁰ proposed the mechanism of a non ionic addition which can be explained by two steps reaction A and B as following:

Step A

Salt reacts with alcohol as solvent to give the acetalkoxymercuric (2).

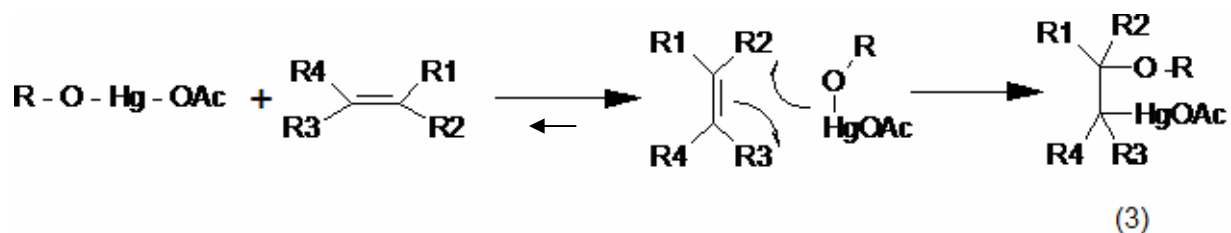


(2)

Scheme-2

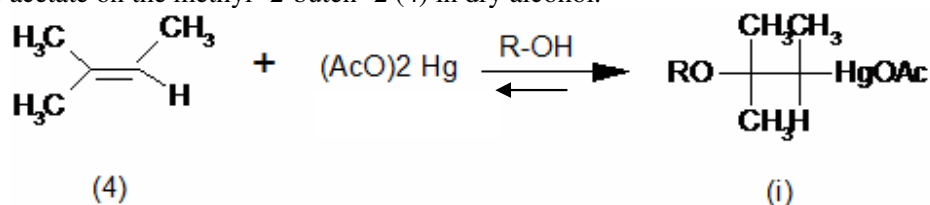
Step B

The obtained products (2) react slowly with the alkenes by a non ionic attack (*cis* addition) to give compounds (3).



Scheme-3

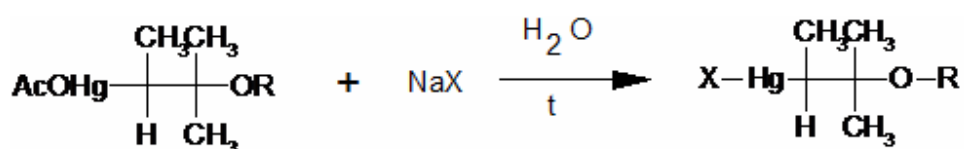
On this basis we have synthesized some acetomeric-3 alkoxy-2-methyl-2 butane (i) by the addition of mercuric acetate on the methyl-2-buten-2 (4) in dry alcohol.



i(1)	i = (1)	R = CH ₃	Rt = 80%
i(2)	i = (2)	R = CH ₃ - CH ₂	Rt = 72%

Scheme-4

Followed by a nucleophilic substitution¹¹ with NaX (X- Br, SCN) of acetoxy group of product (i) in water to obtain mercuric derivatives respectively (j).



j(1) :	1 : R = CH ₃	, X = Br
j(2) :	2 : R = CH ₃	, X = SCN
j(3) :	3 : R = CH ₃ CH ₂	, X = Br
j(4) :	4 : R = CH ₃ CH ₂	, X = SCN

Scheme-5

The products acetomeric-3 alkoxy-2 methyl-2 butane (i) and their derivatives (j) are obtained as solids in a range of yield between 60 and 80%. Those compounds are kinetically and thermodynamically instable.¹¹ We have not used the coupling constant ($J_{\text{Hg-CH}}$) in ¹HNMR because there is not vicinal proton at mercury.

To confirm products (i) and (j), we have used the ^1H NMR spectra which indicate the different protons. The presence of mercury is proved by the mass spectra and Nessler solution. The use of infrared spectra reveals the major functional groups present in the obtained compounds.

A complementary structures conformation are illustrated in Table-1. In which yield R % , melting point f ($^{\circ}\text{C}$) , IR band (ν) , mass spectra (m/z) , Nessler (NS) for products (i) and (j) are reported.

Table-1

Compound	R%	F($^{\circ}\text{C}$)	NS	IR (ν) Cm^{-1}		MS (m/z)		
				C=O	C-O-C	Hg $^{+}$	HgX $^{+}$	X $^{+}$
i (1)	80	35	+	1200	1650	202	260	-
i (2)	72	38	+	1200	1650	202	260	-
j(1)	70	45	+	1200	1650	202	260	-
j(2)	60	40	+	1200	1650	202	260	5
j(3)	80	65	+	1200	1650	202	260	79
j(4)	65	60	+	1200	1650	202	260	58

+ Color red brown

CONCLUSION

The couple Hg^{2+}/Hg has an important potential place in the standard potential redox Schell. This chemical propriety in addition to the important Atomic number value of mercuric element makes the organomercurics compounds thermodynamically and often kinetically instable .This pronounced organomercurics chemical instability could be explored to make intermediate agents which can be used in the synthesis of important pure organic compounds .for this purpose we have carried out this present work.

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[RJC-820/2011]

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