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TURQUIE

Mercuration of Unsaturated β-Bromo Phosphonite And α-Chloro Phosphonate

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SUMMARY

Diethyl (2- bromo -1- phenyl, vinyl) phosphonite and diethyl (1- chloro -1- phenyl, vinyl) phosphonate were allowed to react with mercuric acetate at different conditions inorder to combine the organophosphorus and organomercuric compounds into one molecule and to study the effect of the vinyl group on the stability of P-C bond. Different mercurated products were obtained, some of them were due to cleavage of P-C bond with the formation of mercurated aliphatic phosphonites and phosphonates and the others were formed through substitution and addition reactions.

INTRODUCTION

In earlier work trials have been made by Seyferth *et al*[1] to mercurate dimethyl benzylphosphonate were not successful. In the same year Awad *et al*[2] reported that the mercuration of dialkyl benzylphophonate with mercuric acetate gives benzylacetate and dialkyl phosphonyl mercuric acetate. The mercuration of dialkyl phenylphosphates in which the good leaving benzyl group is replaced by the more resistant phenoxy group, gives alkyl acetate.[3]

Recently El-Sawi *et al*[4] found that the presence of the NO_2 group in dialkyl p-nitrophenyl phosphate facilitated the cleavage of Ar — O—P, while the presence of methyl, hydroxyl, naphthyl, and quinolinyl[5] moeity hindered the cleavage.

Kazankova *et al*[6] found that the reaction of complex mercuric chloride with triisopropyl phosphite and an alkoxy or alkoxyalkylacetylene leads to the formation of a new class of heteroorganic compounds, β-mercurated (1- alkoxyvinyl) phosphates.

In the present investigation, mercuration of diethyl (2-bromo-1-phenyl, vinyl) phosphonite where phosphorus is in the trivalent (low oxidation) state and diethyl (1- chloro -1- phenyl, vinyl) phosphonate in which phosphorus is in the quinquevalent (high oxidation) state, with mercuric acetate were carried out at different temperatures, solvents, and ratios of the reactants. The new compounds prepared in this studies, their melting points and their analysis are collected in Table 1.

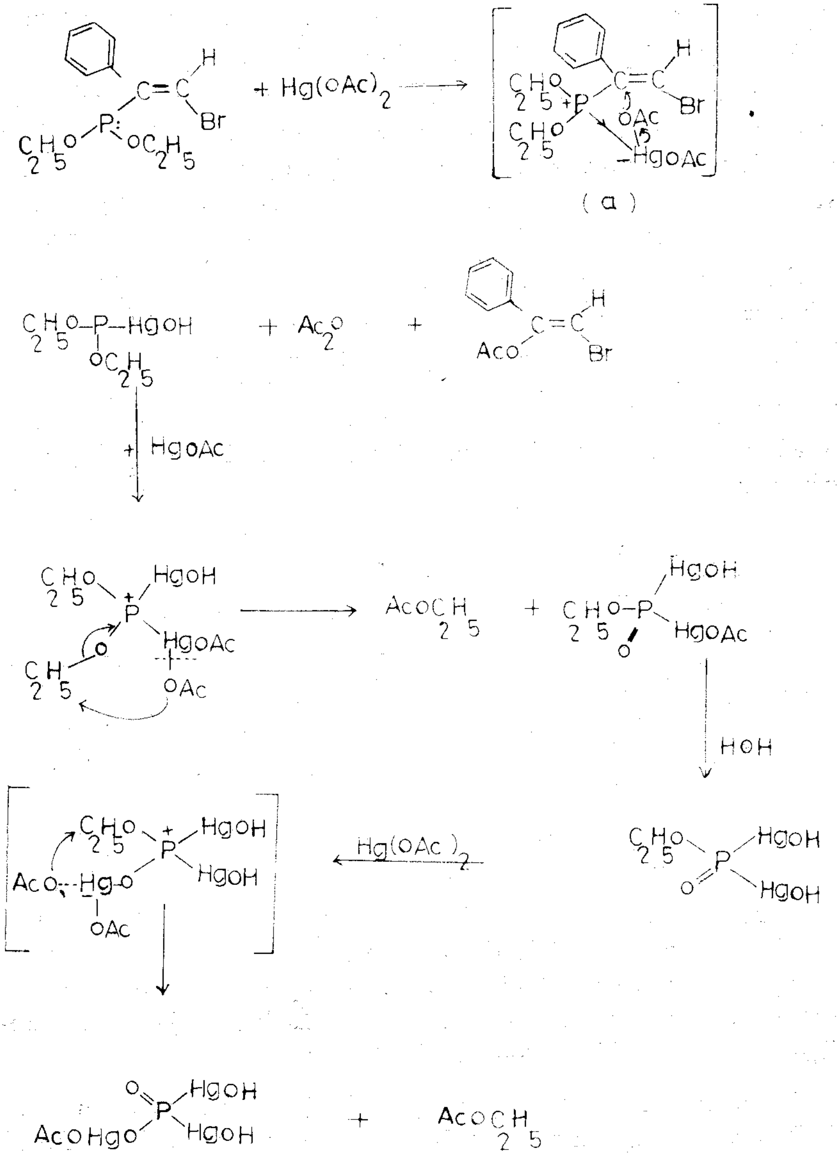
Table I
Mercurated phosphonites. phosphonic acid and phosphonates

Compound	No.	M.p.(°C)	Analysis (calcd.) (%)		
			C	H	Hg
$C_2H_5O_6Hg_3P$	1	d.275°C			79.8 (79.4)
$C_{12}H_{15}O_4BrHgP$	2	80–81°C			37.1 (37.3)
$C_{18}H_{24}O_8BrHg_2P$	3	170–171°C	24.9 (24.5)	2.7 (2.7)	44.9 (45.5)
$C_8H_{10}O_8ClHg_4P$	4	above 300°C			72.5 (72.7)
$C_6H_{11}O_7Hg_2P$	5	above 300°C	10.9 (11.4)	1.9 (1.7)	63.4 (63.9)
$C_8H_8O_5ClHg_2P$	6	d. 300°C	10.2 (10.8)	1.3 (1.2)	67.91 (67.9)
$C_{12}H_{14}O_5ClHgP$	7	94–95°C	30.6 (30.9)	3.6 (3.2)	43.88 (43.13)
$(C_{12}H_{15}O_3ClP)_2Hg$	8	115–117°C	39.1 (38.4)	4.1 (4.2)	27.5 (26.7)
$C_{16}H_{22}O_8ClHg_2P$	9	105–107°C	23.4 (23.7)	2.4 (2.7)	49.8 (49.5)
$C_{14}H_{18}O_5ClHgP$	10	135–136°C	31.00 (31.5)	3.0 (3.2)	37.1 (37.6)
$(C_{10}H_{11}O_3ClP)_2Hg$	11	90–92°C	35.7 (35.15)	3.1 (2.8)	29.0 (29.3)

RESULTS AND DISCUSSION

The reaction of diethyl (2-bromo-1-phenyl, vinyl) phosphonite with mercuric acetate (1/1 molar ratio) in aqueous acetic acid at room temperature gave AcOHgO-P (O) $(HgOH)_2$ in 34.3 % yield.

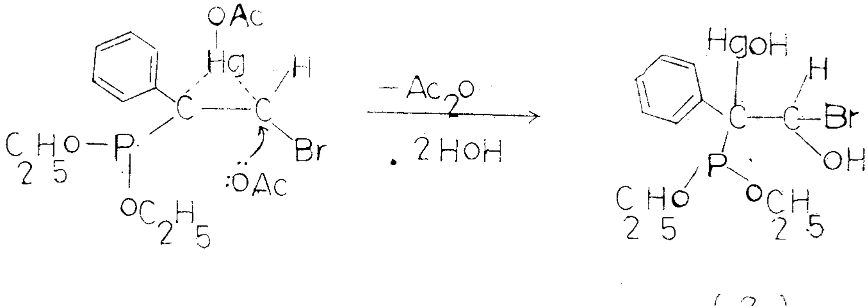
Under this condition it was found that reaction may proceed through an initial formation of intermediate (a) and an intramolecular nucleophilic attack of the carbonyl oxygen on the positively charged carbon atom occurs concomitant with a migration of acetyl group and cleavage of P—C bond.



In this mechanism an intramolecular attack of the acetate group occurs on the alkyl moeity to give the alkyl acetate. This is supported by the fact that the initially formed phosphonium ion R—O—P^+ bond is easily decomposed (Arbusov reaction[7]).

Mercuration of diethyl (2-bromo-1-phenyl, vinyl) phosphonite with mercuric acetate (1/3 molar ratio) gave the same product (1) in 98 % yield. The infra red spectra show absorption bands attributed to $\upsilon_{P=O}$ at 1340 cm^{-1}, υ_{OH} at 3650-2800 cm^{-1}, υ_{P-O-Hg} at 1400 cm^{-1}, while υ_{P-O-C} (aliphatic) at 986, 1052 cm^{-1} completely disappeared.

The reaction of diethyl (2-bromo-1-phenyl, vinyl) phosphonite with mercuric acetate (1/1 molar ratio) in toluene and acetic acid at 100°C gave two mercurated products, the predominant one was AcOHg-O—P (O) $(HgOH)_2$ (1) in 65 % yield, while the other product was $([C_2H_5O]_2P)$ $(C_6H_5—)$ (HgOH) C—CH (OH) (Br) which was obtained via addition reaction on the double bond accompained or followed by hydrolysis.



(2)

Using (1/3 molar ratio) of the reactants in toluene and acetic acid at 100°C gave rise to mainly the product (1) in 65 % yield and a mercurated product due to addition reaction on the double bond and electrophilic substitution reaction in the aromatic ring, $([C_2H_5O]_2P)$ $(AcOHg—C_6H_4—)$ (AcOHg) C—CH (OAc) (Br) (3).

The infra red spectrum of compound (2) showed the characteristic (OH) stretching band at 3600-2550 cm^{-1} (broad band attributed to hydrogen bonding), absorption band at 1160 cm^{-1} can be assigned to the P—O—C_2H_5 assymetric strecthing frequency and the band at

1000–986 cm^{-1} may be assigned to the symmetric stretching frequency of the P—O—C_2H_5. The absorption bands at 750-500 cm^{-1}; 770-730 cm^{-1}, 690 cm^{-1} are attributed to υ_{C-Br} and monosubstituted aromatic. The i.r. spectrum of compound (3) is in good agreement with the suggested structure.

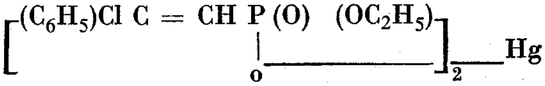
Diethyl (1-chloro-1-phenyl, vinyl) phosphonate reacted with mercuric acetate (1 /1 molar ratio) in aqueous acetic acid at room remperature with the formation of

(HOHg) (HOHg—C_6H_4—) Cl C—CH (OH) [P (O) $(OHgOH)_2$](4) in 24 % yield. The i.r. spectrum showed $\upsilon_{P=O}$ at 1310–1225 cm^{-1} υ_{OH} at 3150-2800 cm^{-1}, υ_{C-Cl} at 800-610 cm^{-1}, υ_{P-O-Hg} at 1400 cm^{-1}.

In the case of (1 /3 molar ratio) in aqueous acetic C_2H_5O—P (O) (HgOAc) (OHgOAc) (5) and (HOHg—C_6H_4—) CI C=CH [P(O) (OH) (OHgOH)] (6) were obtained. The former (5) is the predominent in 63 % yield, identical with an authenitc sample prepared according to Awad *et al*[2]. The i.r. spectrum of compound (6) showed $\upsilon_{P=O}$ at 1330 cm^{-1} (shifted towards higher frequency), $\upsilon_{P<^{O}_{OH}}$ at 1240-1180 cm^{-1}, υ_{C-Cl} at 790-685 cm^{-1}, υ_{OH} at 3600-2800 cm^{-1} and the absorption bands for substituted aromatic.

The reaction of (1 /1 molar ratio) was carried out in toluene and acetic acid at 100°C and gave product (5)

(C_6H_5—) Cl C=CH [P(O) (OC_2H_5) (OHgOAc)] (7) and mercuribis (diethyl 1-chloro-1- phenyl, vinyl) phosphonate (8) in 23 %:23.75 %: 24.1 %. while the reaction products of (1 /3 molar ratio) in toluene and acetic acid were identified to be (5), (AcOHg-C_6H_4—) (HgOAc) Cl C—CH (OH) [P(O) $(OC_2H_5)_2$] (9), (AcOHg—C_6H_4) (CI) C=CH [P(O) $(OC_2H_5)_2$] (10) and



$$\left[(C_6H_5)Cl\,C=CH\,\underset{O\text{———}}{\overset{|}{P}}(O)\,(OC_2H_5)\right]_2\text{—}Hg$$

(11) in 23 %: 24 %: 23 % yield.

EXPERIMENTAL

Analysis: Mercury was determined by mercurimetric procedure against sodium chloride, using diphenylcarbazone as indicator[8].

Procedure I

Acetoxymercuri-dihydroxymercuri phosphonite (1)

A solution of 3.03 g (0.01 mol) of diethyl (2-bromo-1- phenyl, vinyl) phosphonite[9] and 3.18 g (0.01 mol) of mercuric acetate in 25 ml aqueous acetic acid was stirred for 3 hrs. A white crystalline product separated out, filtered off, and rectystallised from acetic acid to give a total of 2.5 g (34.8 %) m.p. 275°C (d).

Mercuration of diethyl (2-bromo-1-phenyl, vinyl) phosphonite with mercuric acetate (1/3 molar ratio) in aqueous acetic acid.

Procedure I was followed for the reaction of 3.03 g (0.01 mol) diethyl (2-bromo-1-phenyl, vinyl) phosphonite with 9.54 g (0.03 mol) in 25 ml. The product was identified to be acetoxymercuri-dihydroxymercuri phosphonite (1) in 7.5 g (98 %) m.p. 275°C (d.).

Procedure II

Mercuration of diethyl (2-bromo-1- phenyl, vinyl) phosphonite with mercuric acetate (1/1 molar ratio) in toluene at 100°C.

A suspension of 3.18 g (0.01 mol) of mercuric acetate in 10 ml toluene was treated at room temperature with a solution of diethyl (2-bromo-1-phenyl, vinyl) phosphonite in 10 ml toluene, 5 ml Acetic acid was added. The reaction mixture was heated at 100°C for 3 hrs. A white crystalline precipitate seperated out during heating, filtered off and recrystallised from acetic acid 5 g (65 %) m.p. 275°C (d.) and was identified to be acetoxymercuri-dihydroxymercuri phosphonite (1). The mother liquor was evaporated at reduced pressure and the residue was crystallised from toluene, petroleum ether 40-60° in 1.7 g (32 %) m.p. 80-81°C and was identified to be diethyl (2-bromo-2-hydroxy-1- phenyl -1- hydroxmercuri, vinyl) phosphonite (2).

Mercuration of diethyl (2-bromo-1-phenyl, vinyl) phosphonite with mercuric acetate (1/3 molar ratio) in toluene at 100°C.

Procedure II was followed for the reaction of diethyl (2-bromo-1-phenyl, vinyl) phosphonite 3.03 g (0.01 mol) with mercuric acetate 9.54 g (0.03 mol). The white precipitate which seperated out during heating was identified to be acetoxymercuri-dihydroxymercuri phosphonite (1) 5 g (65 %).

The mother liquor was evaporated at reduced pressure and the residue crystallised from ether petroleum ether 40-60°C to give 2.9 g (32 %) m.p. 170-171°C which identified to be diethyl (2-bromo-2-acetoxy-1- acetoxymercuri-1- acetoxymercuriphenyl, vinyl) phosphonite(3). Mercuration of diethyl (1-chloro-1- phenyl, vinyl) phosphonate with mercuric acetate (1 /1 molar ratio) in aqueous acetic acid.

The reaction of diethyl (1-chloro-1-phenyl, vinyl) phosphonate[10] 2.7 g (0.01 mol) with mercuric acetate 3.18 g (0.01 mol) was carried out using procedure I.A white precipitate seperated out, filtered off and recrystallised from acetic acid. It was identified as dihydroxymercuri (1-chloro-1-hydroxymercuri-1- hydroxymercuriphenyl, vinyl) phosphonatc (4) 2.7 g (24 %) m.p. above 300°C.

Mercuration of diethyl (1-chloro-1-phenyl, vinyl) phosphonate with mercuric acetate (1 /3 molar ratio) in aqueous acetic acid.

Procedure I was followed. A white precipitate seperated out, filtered off and crystallised from acetic acid to give ethyl (diacetoxymercuri) phosphonate (5) 4 g (63.8 %) m.p. above 300°C. The mother liquor was evaporated under reduced pressure and the residue was crystallised from toluene-petroleum ether 40-60°C to give hydroxymercuri (1-chloro-1-hydroxymercuriphenyl, vinyl) phosphonic acid (6) 1.2 g (32.3 %) m.p. 300°C (d).

Mercuration of diethyl (1-chloro-1-phenyl, vinyl) phosphonate with mercuric acetate (1:1 moler ratio) in toluene at 100°C.

Procedure II was followed: A white precipitate seperated out, filtered off and crystallised from acetic acid to give ethyl (di-acetoxymercuri) phosphonate (5) 1.5 g (23 %) m.p. above 300°C.

The mother liquor was evaporated. The remaining oily product was treated with ether whereby a crystalline solid was seperated out, filtered off and crystallised from toluene-petroleum ether 40-60°C. The product was identified to be ethyl acetoxymercuri (1-chloro-1-phenyl, vinyl) phosphonate (7) 1.9 g (23.8 %) m.p. 94-95°C.

The mother liquor (the etherial layer) was then evaporated to obtain crystalline product, recrystallised from toluene-petroleum ether 40-60°C to give yellow crystals. It was identified to be mercuri bis (1-

phenyl-1- chloro, vinyl diethyl phosphonate) (8) 0.89 g (24 %) m.p. 115-117°C.

Mercuration of diethyl (1-chloro-1-phenyl, vinyl) phosphonate with mercuric acetate (1/3 molar ratio) in toluene at 100°C.

The same procedure II was followed. The white precipitate was filtered off and crystallised from acetic acid. Identified to be ethyl diacetoxymercuri phosphonate (5) 1.5 g (23 %) m.p. above 300°C.

The filterate was treated with ether to obtain crystalline solid product, filtered off and recrystallised from toluene petroleum ether 40-60°C to give diethyl (1-chloro-1-acetoxymercuriphenyl-1- acetoxymercuri-2- hydroxy, vinyl) phosphonate) (9) 2 g (24 %) m.p. 105-107°C.

The above mother liquor was then concentrated under reduced pressure to give crystalline solid, filtered off and crystallised from toluene-petroleum ether 40-60°C to give diethyl (1-chloro-1-acetoxymercuriphenyl-cinyl) phosphonate (10) 1.3g (24 %) m.p. 135-136°C.

The filterate was then evaporated under reduced pressure to give mercuri bis ethyl (1-chloro-1-phenyl, vinyl) phosphonate (11) 0.8 g g (23 %) m.p. 90-92°C.

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