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Preliminary communication

The reaction of vinyl halides with mercury(II) salts

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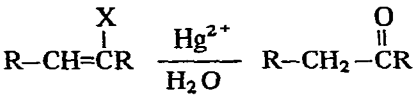
SUMMARY

The reaction of vinyl halides with mercuric salts in water to give the corresponding carbonyl compounds is non-catalytic, and the postulated mechanism includes an oxymercuration-dehalogenation step.

Reactions of transesterification and transetherification of vinyl esters and vinyl ethers catalysed by mercuric salts have been known for a long time[1,2]. The intensive work presently underway on the mechanism of nucleophilic substitution at a vinylic carbon[3] brought up a renewed interest, leading to a thorough scrutiny of these reactions[4,5].

We wish now to report the results of the closely-related reaction of vinyl halides with mercuric salts which affords the corresponding carbonyl compound according to eqn. (1).



$$\text{R–CH=}\overset{\displaystyle X}{\overset{|}{\text{C}}}\text{R} \xrightarrow[\text{H}_2\text{O}]{\text{Hg}^{2+}} \text{R–CH}_2\text{–}\overset{\displaystyle O}{\overset{\|}{\text{C}}}\text{R} \qquad (1)$$

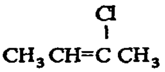
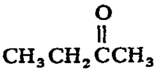
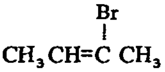
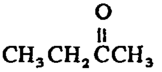
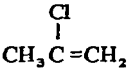
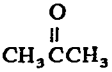
X = Cl, Br

A summary of the yields obtained with various olefins and mercury salts is given in Table 1.

This reaction differs from that of simple olefins as it does not constitute a redox process[6] since the mercuric species are not reduced. Furthermore, contrary to the mercury(II)-catalysed hydrolysis of isopropenylacetate, the stoichiometry of the reaction

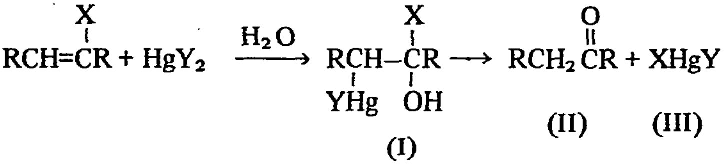
TABLE 1

PRODUCTS FROM THE REACTION OF VINYL HALIDES WITH VARIOUS MERCURY(II) SALTS IN H_2C AT 60°.

Vinyl halides	*Products*	*Mercury salts and yields (%)* [a]			
		$Hg(ClO_4)_2$	$HgSO_4$	$Hg(NO_3)_2$	$Hg(BF_4)_2$
 $CH_3CH{=}\overset{Cl}{\overset{\vert}{C}}CH_3$	 $CH_3CH_2\overset{O}{\overset{\Vert}{C}}CH_3$	71	69	74	67
 $CH_3CH{=}\overset{Br}{\overset{\vert}{C}}CH_3$	 $CH_3CH_2\overset{O}{\overset{\Vert}{C}}CH_3$	50	55	59	51
 $CH_3\overset{Cl}{\overset{\vert}{C}}{=}CH_2$	 $CH_3\overset{O}{\overset{\Vert}{C}}CH_3$	91	93	96	89

[a] By GLPC analysis.

shows clearly its non-catalytic character. In spite of this difference however, a similar oxymercuration-dehalomercuration mechanism can be involved for the reaction of vinyl halides (eqn. 2).



$$RCH{=}\overset{X}{\overset{\vert}{C}}R + HgY_2 \xrightarrow{H_2O} \underset{\underset{YHg}{\vert}}{RCH}-\underset{\underset{OH}{\vert}}{\overset{X}{\overset{\vert}{C}}}R \longrightarrow \underset{(II)}{RCH_2\overset{O}{\overset{\Vert}{C}}R} + \underset{(III)}{XHgY} \qquad (2)$$

(I)

X = Cl, Br
Y = ClO_4, SO_4, NO_3, BF_4

The non-catalytic character of the process most probably resides in the nature of the eliminated mercuric species(III) which lacks the ability to add to a second molecule of vinyl halide.

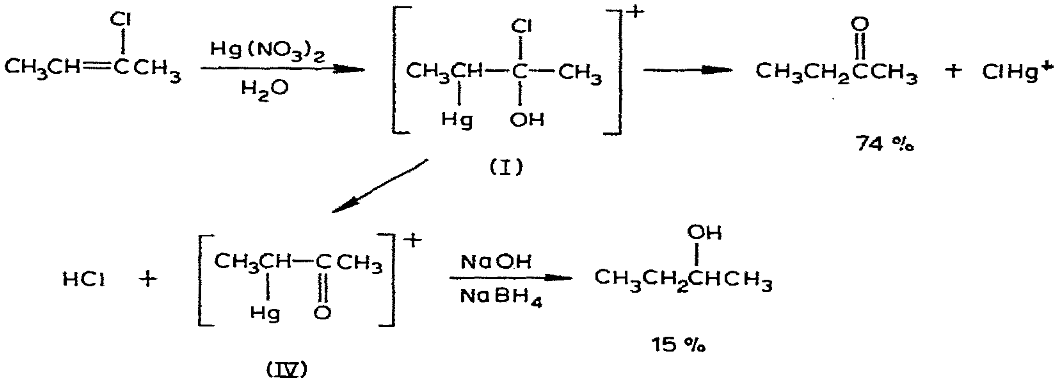
This inhibitory role of the halide ion is shown in the hydrolysis reaction of vinyl esters. Thus the mercury(II)-catalysed formation of acetone from isopropenylacetate[4,5] was greatly slowed down when the reaction was carried out in the presence of sodium chloride. Furthermore, the inability of a $ClHg^+$ species to add to an olefin was established when $HgCl_2$ was found to be inactive towards 2-chloro-2-butene. These results are in agreement with the well-known property of halide ions to shift the equilibrium of oxymercurials towards the free olefin in acidic medium[7,8].

These results led us to test the feasibility of the proposed mechanism, involving oxymercuration-deoxymercuration, for the vinyl interchange in mercury(II)-catalysed transesterification and transetherification[1,2]. According to our observation a distinct catalytic

(3)

inhibition should have been obtained with halide ions. Indeed, we found that a typical reaction giving excellent yield of transesterification[9] gave, in the presence of KCl(Hg^{2+}/Cl^- = 0.5), but otherwise under identical experimental conditions, only trace amounts of products. This provides additional support to the addition–elimination mechanism and definitely discards the previously suggested[10] path involving an acetylene–mercury complex intermediate, since halomercuric species react readily with alkynes[11].

One must point out however that the path shown in eqn. 1 is not unique, as may be concluded from the yields given in Table 1. The intermediate addition product (I) may also undergo an HX elimination to yield a stable β-ketomercurial (IV). This alternative route was tested by reducing the reaction mixture, free of organic products, using basic sodium borohydride. For example, 2-chloro-2-butene reacted with mercuric nitrate to give 70% of methyl ethyl ketone. Distillation of the unreacted olefin and the ketone formed afforded a suspension which, when rendered basic and reduced with sodium borohydride, yielded 15% of 2-butanol.



Further experiments using a wide variety of vinyl halides in various media are in progress in order to identify the proposed intermediates.

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