Bull. Inst. Chem. Res., Kyoto Univ. Vol. 50, No. 3, 1972

Effects of Anions of Mercuric Salts in Oxymercuration

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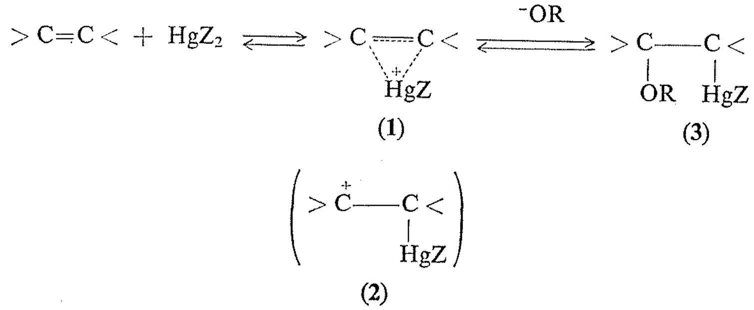
Received May 29, 1972

It has been well known that mercuric salts readily react with olefins in hydroxylic solvents giving oxymercurials, in which mercuric ions and the solvents add to a double bond making a covalent bond between carbon and metal.



It is widely accepted that the oxymercuration reaction of simple olefins takes place in a stereospecific *trans* fashion and the orientation is in accord with the Markovnikov's rule, that is, by placing the mercury atom on the carbon atom having the more hydrogen.[1] While the stoichiometry and stereochemistry of the reaction have been extensively investigated, the mechanism of the reaction, especially the structure of the reaction intermediate, is still left uncertain. A symmetrically bridged mercurinium ion (**1**) has been postulated as an intermediate in oxymercuration and acid-induced deoxymercuration reactions.[2] Furthermore, Olah recently reported the direct observation of these ions in FSO_3H—SbF_6—SO_2 solution by N.M.R.[3] These evidences, however, can not utterly exclude the possibility that the oxymercuration proceeds *via* a mercuricarbonium ion (**2**) in less acidic conditions.[4]

In connection with the foregoing discussion on the intermediate, little is yet known of the effect of the anions of mercuric salts in the oxymercuration reaction.

In this paper we report the results on such effect in the oxymercuration reaction of styrene with several kinds of mercuric salts in aqueous tetrahydrofuran solution. Recently Brown reported a convenient mild procedure for the oxymercuration of olefins and sodium borohydride demercuration, and also that undesirable side reactions such as polymerization, oxydation and substitution did not appear to be important under the

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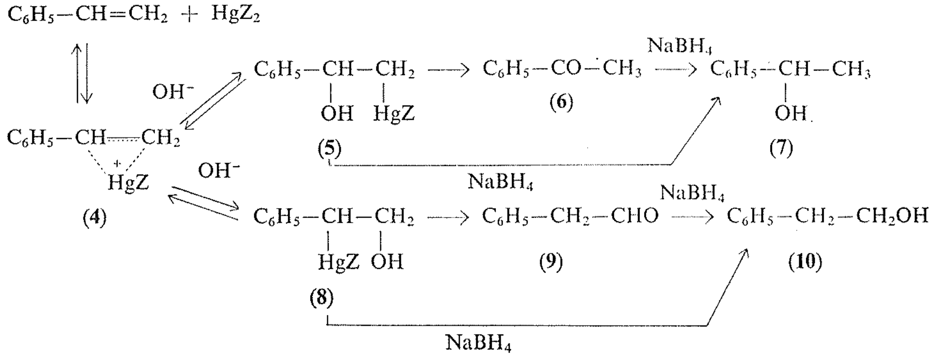
conditions adopted.[5] Consequently, utilizing these procedures we attempted to prove the effects of anions on oxymercuration reaction of styrene with mercuric acetate, trifluoroacetate and perchlorate.

Styrene was subjected to oxymercuration reaction with equivalent amount of mercuric salts in aqueous tetrahydrofuran (1:1) solution at room temperature (*ca.* 25°), the produced oxymercurials were submitted to demercuration *in situ* with alkaline sodium borohydride. The products were analyzed by v.p.c. The results are shown in Table 1.

Table 1. Results of Oxymercuration-demercuration of Styrene with HgZ_2 in $THF-H_2O$ (1:1).

Run	Z	Reaction time		Yield of	
		Oxymercuration	$NaBH_4$ Reduct.	**7** (%)	**10**/(**7**+**10**) (mole %)
1	CH_3COO	25 min.	25 min.	94.5	0.045
2		180	20	95.9	0.084
3	CF_3COO	25	20	58.9	0.16
4		60	20	61.0	0.44
5		60	60	57.9	0.45
6		180	20	68.1	0.49
7	ClO_4	5	20	90.2	0.32
8		25	20	74.8	0.91
9		60	20	87.6	0.83
10		180	20	90.3	1.53

Many earlier investigations of oxymercuration of olefins have established that the *addition proceeds in a Markovnikov manner, and that for simple unhindered olefins,* addition is *trans*. Although it was as a matter of fact in our results, the amounts of the by-produced 2-phenylethanol (**10**) were varied with both the anions of mercuric salts and reaction time. The amount of 2-phenylethanol increased with the increase of the ionic character of the salts. On the other hand, the amount of 2-phenylethanol increased by prolonging the reaction time using any of those mercuric salts. On comparison between the results of runs 4 and 5, the difference evidently seems to have occurred in the process of oxymercuration, not of the reductive demercuration. The fact that the amount of 2-phenylethanol increased by prolonging the reaction time is accounted for if 1-phenylethanol (**7**) is a kinetically controlled product of the reaction and 2-phenyl isomer is a thermodynamically controlled rearrangement product. The rearrangement from 1-phenylethanol to 2-phenyl substituted one, however, is contrary to the usual rearrangements, and it seems difficult to explain these phenomena by classical carbonium ion mechanisms. The fact that the increase of the anti-Markovnikov type alcohol, 2-phenylethanol, by increasing of ionic character of mercuric salts in the present case, and also that the apparent rearrangement from 1- to 2-phenylethanol, appears to be suggestive of the presence of the mercurinium ion as an intermediate. That is, the increase of the ionic character of mercuric salts seems to stabilize the bridged mercurinium ion in the due course, for such bridged ion was detected in the super-acidic solution as an extreme.[3] The attack of hydroxide anion upon the β-position of the styrene mercury complex is facilitated by stabilization of the mercurinium ion intermediate (**4**). The oxymercuration process is reversible as well known, then the formation of 2-phenylethanol is also understandable as a thermodynamically controlled product.



On the other hand, the oxidation of olefins by mercuric salt was reported by Strini,$^{6)}$ where propene was oxidized by Hg^{2+} salts in aqueous sulfuric or perchloric acid solutions obtaining a small amount of acetone and propanal in addition to acrolein as a major product. If an analogous oxidation proceeds in the present case, acetophenone (**6**) and phenylacetaldehyde (**9**) may be produced although the reaction temperature has been much lower than that presented by Strini. These oxidation products are reduced by sodium borohydride to give 1- (**7**) and 2-phenylethanol (**10**) which are unfortunately unidentified from the direct reductive demercuration products of the oxymercurials (**5** and **8**).

The mechanism of the reaction of oxidation of propene by mercuric salts in aqueous acid solution has been proposed as that it involves the formation of an olefin π-complex and hydroxy-mercuric addition compounds, oxymercurials, which lead to the formation of acetone and propanal, and also involves the formation of an allylic π-complex, which leads to acrolein. Supposing 2-phenylethanol (**10**) is the product through oxidation process, it is convincing that the more acidic mercuric salts resulted the higher yields of 2-phenylethanol and that the amount of 2-phenylethanol also increased on prolonged reaction, if the rate of reaction **8** to **9** is greater than that of reaction **5** to **6**. If phenyl migration, and not hydride shift, occurred in these oxidation processes, the results should be opposed to the discussion mentioned above. However, such phenyl migration is improbable in the oxidation of oxymercurials.$^{7)}$

The clear estimation has not been obtained at the present stage of experiments by which process 2-phenylethanol was obtained, by direct demercuration of oxymercurial or *via* oxidation and reduction process. Much further work is needed before any worthwhile conclusion can be drawn to the reaction mechanism involved.

EXPERIMENTAL

Materials. Commercially available mercuric acetate was used without further purification. Mercuric perchlorate (hydrate) was also a commercial product and used after determining the mercuric content by titration. Mercuric trifluoroacetate was prepared by the method of Brown.5) Styrene and tetrahydrofuran were distilled before use in each experiment.

General oxymercuration-demercuration procedure. Mercuric acetate (3.19 g: 10 m-mole) was dissolved in 10 ml of water, to which solution was added 10 ml of tetrahydrofuran. Then 1.04 g (10 m-mole) of styrene was added dropwise to the solution under well-stirring at 24.2–25.8 °, and stirring was continued for 3 hr at that temperature. After the duration, 10 ml of 3.0 *M* NaOH was added, followed by 10 ml* of 0.5 *M* sodium borohydride in 3.0 *M* NaOH and the reaction was carried on for 20 min.

The reaction mixture was saturated with sodium chloride, and extracted twice with 15 ml of ether each. The combined extract was washed with saturated sodium chloride solution and dried over $MgSO_4$. After removal of the solvent, *ca.* 1.5 ml of the product was obtained.

Analysis. The alcohol products were identified by comparison of v.p.c. retention times with those of authentic samples of the alcohols. Calculations of yields were made on the basis of unreacted styrene and the products as determined by integration of peaks obtained from solutions of authentic samples and the products. The absolute values of percentage of 2-phenylethanol are unable to be expected with high accuracy since the integration of peaks was obtained by changing the attenuation of gas chromatograph, however, the relative values of each run were reliable within 10% errors (av. 5.9%). Analyses were carried on Shimadzu GC–3AH gas chromatograph with PEG-20M 3 m column.

In the case of runs 2 and 10, a small amount of benzaldehyde (less than 1.5%) and benzyl alcohol (trace) was detected as by-products. Benzaldehyde was derived to its 2,4-dinitrophenylhydrazone and identified by comparison of IR spectrum with that of the authentic sample.

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* In the case of perchlorate, 20 ml of the solution was added.