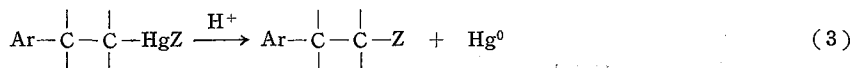
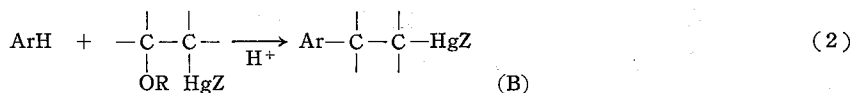
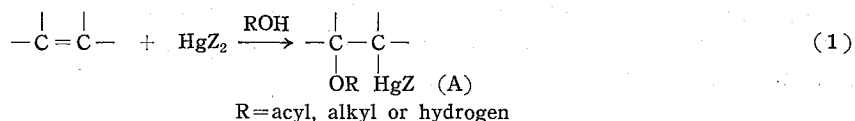


ICHIKAWA LABORATORY (July 1958~)

Head: Dr. Katsuhiko Ichikawa

In 1958, Ichikawa Laboratory was founded to conduct the basic research in the field of petroleum chemistry. The major interest has been oxymetallation and its application to organic synthesis. Chemical and spectroscopic studies of cyclopropane derivatives, mechanism of acylation in basic media and stereospecific synthesis have been also under investigation.

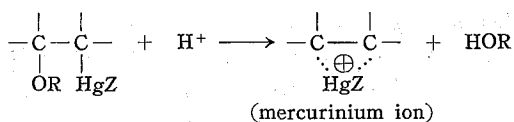
In various solvents, it was found that olefins react with aromatics to form β -arylethyl alcohols or their esters in the presence of mercuric salt and strong acid. That is a new type of alkylation and a convenient synthetic method of preparing alcohols or esters substituted with aromatics at β -position. The reaction was found to proceed through the following mechanism:



Under milder conditions, the intermediate mercurials (B) were isolated in good yields. This means that alkylbenzenes containing mercury at β -position can be prepared conveniently by the reaction of oxymercurials (A) with aromatics in the presence of strong acid.

This synthetic method of preparation of mercurials has been extended to various active methylene compounds successfully. For example, 3,3-diacetylpropylmercuric chloride was obtained by the reaction between acetylacetone and oxymercurial of ethylene and subsequent treatment of the product with hydrochloric acid.

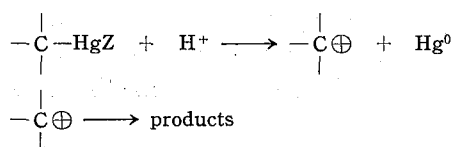
The reaction of oxymercurials with aromatics is second-order. From the results of kinetic studies on the effects of the structure of olefins, substituents of the aromatic ring and the acidity function of the reaction media, it was concluded that the reaction is a kind of electrophilic aromatic substitution of mercurinium ion which is formed from the oxymercurial by the reaction with strong acid.



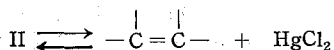
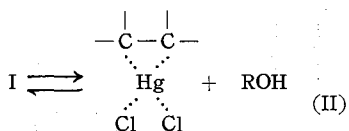
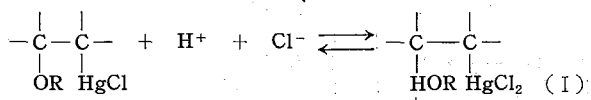
The rate determining step is the reaction of this mercurinium ion with the aromatics.

The structures of the isomers formed can be explained reasonably by this mechanism. The reactivity of the mercurinium ion from ethylene as an electrophilic reagent is about the same with that of nitronium ion.

The demercuration of mercurials by equation 3 is an unusual reaction as organo-metallics. Kinetic studies, particularly the effects of the acidity function on the rates revealed that the reaction proceeds through the following mechanism:



The mechanism of oxymercuration is still ambiguous, although many investigations have been conducted since this reaction was reported in 1899 for the first time. Hydrohalogenic acids decompose the oxymercurials very easily, while oxyacids only slowly. The former does not catalyze the reaction by equation 2. To investigate these points, the decomposition of oxymercurials with hydrochloric acid was studied kintetically. The reaction is third-order, and the mechanism was found to be as follows:



The mercurials obtained by the reaction of oxymercurials with β -diketones showed unusual chemical behavior which is interesting as the method of preparing cyclopropane derivatives and as a mechanistic problem. For example, treatment of 3,3-diacetylpropylmercuric chloride with aqueous potassium hydroxide gave 1,1-diacetylcyclopropane as the only isolable organic product. Demercuration of the acetate of the same compound with perchloric acid gave the same cyclopropane together with other products. The detailed mechanism is under investigation.

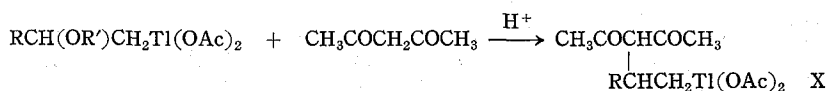
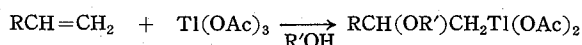
1,1-Diacetylcyclopropanes are the interesting compounds for spectroscopic studies such as ultraviolet and nuclear magnetic resonance, since these are the special type of non-enolizable β -diketone. By u.v. spectroscopy, the problem of conjugation between cyclopropane ring and β -diketo group has been studied.

Oxyplumbation and oxythallation of olefins with lead tetra-acetate and thallic acetate have been studied as the extention of oxymercuration mentioned above.

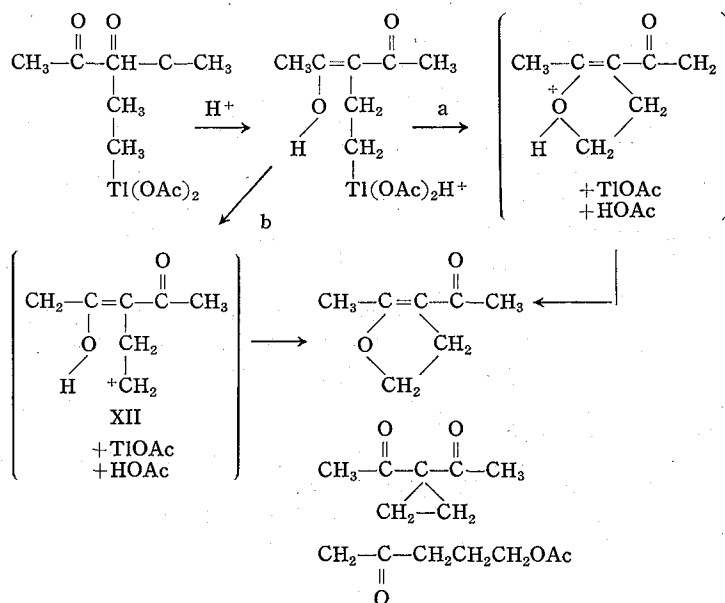
Kinetic studies of the reaction of lead tetraacetate with anethole revealed that a formation of oxyplumbate occurs and the oxidation (formation of diacetate of anethole)

follows and that the oxyplumbation is an equilibrium reaction. Oxidation of various type of olefins, involving those substituted with hetero atoms, with thallic acetate was studied too.

Application of oxyplumbation and oxythallation to organic synthesis was studied also. Condensation of olefins with active methylene compounds took place in the presence of these salts and strong acid. For example, acetylacetone reacted with ethylene to form 3-acetyl-2-methyl-4,5-dihydrofuran as the main product. Although further experiments are required to determine the detailed mechanism, it seems likely that the reaction which is analogous to the case of oxymercurials does proceed. A tentative mechanism was proposed as follows:



When R=H,



Publications

(* indicates an article published in Japanese)

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 15. K. Ichikawa, S. Uemura and T. Sugita: Reaction of Olefins with Acetylacetone in the Presence of Thallic Acetate, *Tetrahedron*, **22**, 407 (1966).
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