

creating their own holes, leaving most of the original holes intact. We therefore believe that loss of holes by compression may possibly be the major factor in the resulting diminution of conductance. Studies are being undertaken using other inert gases at the same pressure and temperature to ascertain if there is any dependence of conductance change on solubility.

DEPARTMENT OF CHEMISTRY
KANSAS STATE UNIVERSITY
MANHATTAN, KANSAS 66504

JAMES L. COPELAND
WALTER C. ZYBKO

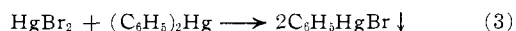
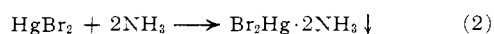
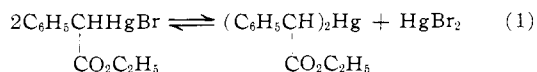
RECEIVED SEPTEMBER 18, 1964

The Mechanism of Symmetrization of Ethyl α -Bromomercuri-phenylacetate by Diphenylmercury

Sir:

Conversion of organomercuric salts to diorganomercuric compounds, termed symmetrization, can be accomplished by a variety of reagents. These transformations occur by diverse mechanisms and represent important electrophilic reactions for mechanism studies.

The symmetrizations of esters of α -halomercuriarylacetic acids have been extensively studied by Reutov and co-workers. Closely similar mechanisms were suggested for symmetrization by ammonia¹ (eq. 1 and 2) and by diphenylmercury (eq. 1 and 3).² Independ-



ent evidence was cited supporting each mechanism. The mechanistic proposals were considered mutually supporting since the first step in each is the same.

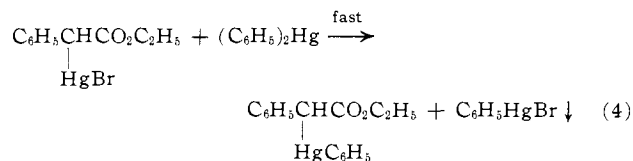
However, the kinetic evidence presented by Reutov and co-workers for the symmetrization by ammonia has been re-examined, and it has been shown that the proposed mechanism (eq. 1 and 2) would not give the observed kinetics.³ The sole remaining evidence offered in support of Reutov's mechanism is the proposal that the reaction with diphenylmercury takes a similar course. A re-examination of this reaction, a summary of which is given here, has revealed that the mechanism proposed by Reutov and co-workers for symmetrization by diphenylmercury is also incorrect.

The reaction of ethyl α -bromomercuri-phenylacetate (0.2 M) with diphenylmercury (0.1 M) was found to proceed in two stages. The first reaction, which is complete in less than 60 sec., yields as a precipitate 1 mole of phenylmercuric bromide for each mole of diphenylmercury. The second reaction requires about two weeks for complete reaction at room temperature and yields a second mole of phenylmercuric bromide.

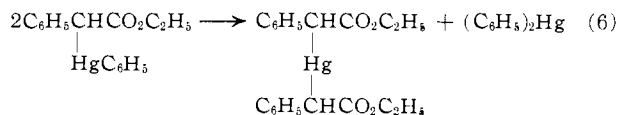
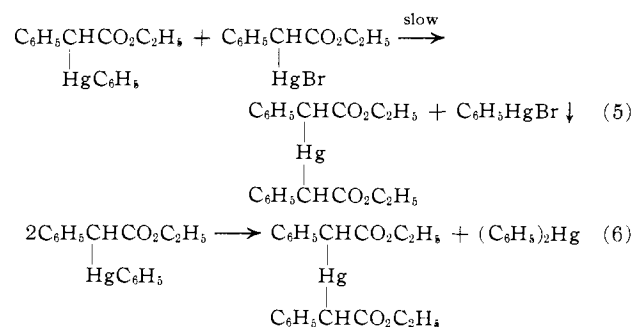
When alkylmercuric salt and diphenylmercury were allowed to react in chloroform solution in mole ratios of

4:1, 2:1, 1:1, and 1:2, the phenylmercuric bromide obtained in the fast reaction was found to correspond (95–99% yield) to the molar quantity of the reagent present in the lesser amount. Therefore, the stoichiometry of the fast reaction is 1:1. This finding negates the mechanism of Reutov and co-workers which requires a stoichiometry of 2:1.

The observed stoichiometry is consistent with formation of unsymmetrical diorganomercurial in the fast reaction (eq. 4). This material is slowly converted to symmetrical dialkyl and additional phenylmercuric



bromide either by eq. 5, or by eq. 6 and another re-



action equivalent to eq. 4.

Additional evidence which strongly supports this scheme was obtained by examination of the n.m.r. spectra of the reaction mixtures. The spectrum of the product obtained in the fast reaction (reagents in 1:1 molar quantities) is different from that of the symmetrical dialkylmercury compound, but is consistent in every respect with the spectrum expected of the unsymmetrical mercurial (eq. 4). The n.m.r. spectrum of the solution slowly changes with time and additional signals appear which correspond to diphenylmercury and the symmetrical dialkylmercurial. The signals of the original spectrum do not entirely disappear, but evidently decrease only until equilibrium is attained. When ethyl α -bromomercuri-phenylacetate and diphenylmercury are reacted in 2:1 molar concentrations, the n.m.r. spectrum of the solution (phenylmercuric bromide precipitates) corresponds to a composite of the spectrum attributed above to the unsymmetrical alkylmercurial and unreacted ethyl α -bromomercuri-phenylacetate. In time, these signals gradually disappear and a new set appears which corresponds to the spectrum of the symmetrical dialkylmercurial.

While the above results indicate the probable sequence of reactions for symmetrization, they do not provide evidence regarding the actual details of bond making and bond breaking.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA

FREDERICK R. JENSEN⁴
JOHN MILLER

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