INVESTIGATION OF THE PRODUCTS OF THE ADDITION OF MERCURY SALTS TO DISUBSTITUTED ACETYLENES

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In a previous paper we have described the addition of mercury salts to dimethyl- and diphenyl-acetylenes [1]. These reactions led to the preparation of new organomercury compounds of the ethylene series. Reaction of 2-butyne (dimethylacetylene) with mercuric acetate yielded three isomeric products, the \( \alpha \), \( \beta \), and \( \gamma \)-isomers melting at 140°, 95°, and 130° respectively. The structures of these isomers were proved by ozonization, and it was shown that the \( \alpha \)- and \( \beta \)-compounds formed a pair of geometric isomers, and the \( \gamma \)-compound was structurally isomeric with these:

\[
\begin{align*}
\text{CH}_3\text{C} &= \text{OCOCH}_3 \\
\text{HgCl} &
\end{align*}
\]

In the same paper we described some of the chemical and physical properties of these compounds.

We now describe a further investigation of the chemical and physical properties of these three compounds. A study of the infrared absorption spectra has enabled us to determine the geometric configurations of the \( \alpha \)- and \( \beta \)-isomers. The absorption spectrum of the \( \alpha \)-isomer (Fig. 1) contains a frequency of 1667 cm\(^{-1}\) in the characteristic region of the \( \text{C}=\text{C} \) bond, whereas the spectrum of the \( \beta \)-isomer (Fig. 2) contains a frequency of 1655 cm\(^{-1}\) in the same region. The spectra contain also a frequency of 1758 cm\(^{-1}\) corresponding to the \( \text{C} \equiv \text{O} \) group, which is present in both compounds.

Hence, a higher \( \text{C}=\text{C} \) frequency was found for the \( \alpha \)-isomer than that found in the same region for the \( \beta \)-isomer. The more highly symmetrical trans compound generally has the higher \( \text{C}=\text{C} \) frequency [2], and for this reason we have ascribed the trans configuration to the \( \alpha \)-isomer, and the cis configuration to the \( \beta \)-isomer. This assignment of configurations is in accord with the fact that the \( \alpha \)-isomer is of lower solubility in organic solvents and has a higher melting point than the \( \beta \)-isomer - most trans compounds are related in this way to the cis isomers.

By the same method we have established the configurations of the symmetrical stereoisomers of bis(2-acetoxy-1-methylpropenyl)mercury. The stereoisomer prepared from the \( \alpha \)-isomers had a \( \text{C}=\text{C} \) frequency of 1621 cm\(^{-1}\) (Fig. 3), whereas its stereoisomer, prepared from the \( \beta \)-isomer, had a \( \text{C}=\text{C} \) frequency of 1616 cm\(^{-1}\) (Fig. 4). On the basis of this difference in frequency we consider that the stereoisomer of bis(2-acetoxy-1-methylpropenyl)mercury of m.p. 114° has the trans-trans configuration, and the other isomer has the cis-cis configuration. The absence of a third stereoisomer having the cis-trans configuration was proved by the fact that the reaction of the trans-trans isomer with mercuric chloride yielded only pure trans-2-acetoxy-1-methylpropenylmercury chloride and the reaction of the cis-cis isomer with the same reagent yielded only cis-2-acetoxy-1-methylpropenylmercury chloride without any trans-isomer as by-product.

It has been shown previously [1] that the \( \alpha \)-, \( \beta \)-, and \( \gamma \)-isomers are readily symmetrized to the corresponding fully substituted organomercury compounds. Each of these three symmetrical compounds (the cis-cis/trans-trans pair and their structural isomer) readily reacts with thallium trichloride in an ether medium, forming the corresponding disubstituted organothallium compound by the equation:

\[
2\left[\begin{array}{c}
\text{CH}_3 \\
\text{H}_2\text{COOCH}_3 \\
m.p. 114°
\end{array}\right] \text{Hg} + \text{TlCl}_3 \rightarrow \left[\begin{array}{c}
\text{CH}_3 \\
\text{H}_2\text{COOCH}_3 \\
m.p. 165°
\end{array}\right] \text{TlCl} + \left[\begin{array}{c}
\text{CH}_3 \\
\text{H}_2\text{COOCH}_3 \\
m.p. 166°
\end{array}\right] \text{HgCl}
\]

*At our request D. N. Shigorin determined the infrared absorption spectra, and we are very much indebted to him for this.*
The organothallium compounds obtained by reactions (1), (2), and (3) are white crystalline substances melting respectively at 166°, 156°, and 196°. They are soluble in alcohol, acetone, and hot water, but insoluble in benzene and ether. In each reaction, in addition to the disubstituted organothallium compound, the corresponding (a, b, or γ) organomercury compound is formed.

The investigation of this reaction revealed that the stereoisomers of bis(2-acetoxy-1-methylpropenyl)mercury differed in their reactivities toward thallium trichloride; the trans-trans isomer is more reactive than the cis-cis isomer obtained from the β-compound. Reaction (1) proceeds instantaneously with evolution of heat, and the reaction product separates as a white crystalline precipitate; the reaction is quite complete in ten minutes. Reaction (2) proceeds more sluggishly without evolution of heat, and 40 minutes is required for its completion. We have thus again observed a difference in the rates at which the cis and trans isomers of organomercury compounds react [3]. We explain this difference by the higher degree of σ-conjugation in compounds in which there is a trans disposition of metal relative to an anionoid group [4].

The high-melting bis(2-acetoxy-1-methylpropenyl)thallium chloride reacts with mercury in acetone and yields the original trans-trans-bis(2-acetoxy-1-methylpropenyl)mercury, m.p. 114°.