REDISTRIBUTION REACTIONS OF SOME BISORGANOMERCURY COMPOUNDS

By

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ABSTRACT

Redistribution equilibria have been studied in a number of binary bisorganomercury systems. The reactions were carried out without catalysts over a wide range of initial system compositions. Gas-liquid chromatography was used to measure equilibrium concentrations of the three components of each system. The attainment of equilibrium was carefully checked, and equilibrium constants for each system were calculated from these concentration data.

The results of redistribution in the systems, diethylmercury/bis(i-propyl)mercury and diethylmercury/bis(n-propyl)-mercury indicated that steric requirements of the exchanging ligands are of minor importance in determining the position of redistribution equilibria.

Electronegativities of the exchanging ligands were shown to exert a major influence on the position of redistribution equilibria from consideration of the results in the systems:

bis(i-propyl)mercury/bis(perfluoro-i-propyl)mercury and bis(n-propyl)mercury/bis(perfluoro-i-propyl)mercury.

Resonance interaction capabilities and ligand carbon orbital hybridization were also shown to be pertinent factors by consideration of the results for the systems: diethylmercury/bis(n-propyl)mercury, diethylmercury/divinylmercury, diethylmercury/diphenylmercury, and diethylmercury/bis(cyclopropylmercury.

From the equilibrium constants determined for the systems studied, equilibrium constants were predicted for a number of uninvestigated systems.

Possible extensions of the results of this study to systems of other metals are discussed in the "Interpretation of Results" section.

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INTRODUCTION

The inorganic chemist is almost daily confronted with some problem connected with lability, the tendency of certain compounds to interchange ligands or substituents. Lability of inorganic compounds may be in part responsible for the fact that the chemistry of carbon, which forms relatively inert compounds, is more fully developed than that of other elements. In any case, knowledge of the characteristics of these exchange processes appears to be prerequisite to the understanding of the nature of inorganic molecules.

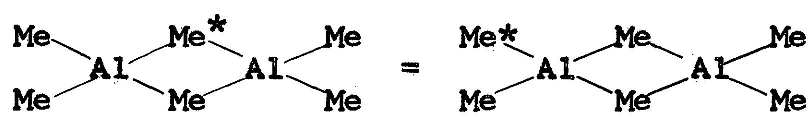
The importance of the consideration of such processes is exemplified in the current controversy concerning the structure of the well-known Grignard reagent. Some researchers (1) believe that the conventional Grignard solution, RMgX, can be best represented as an equilibrium exchange system of the type

$$R_2Mg + MgX_2 = 2\ RMgX$$

Other investigators contend that this exchange reaction does not occur and that the species RMgX does not exist. They report (2, 3) instead that the Grignard solution is an exchange system of the type

$$R_2Hg + MgX_2 = R_2Hg \circ MgX_2$$

The fact that both these views are apparently supported by certain evidence is indicative of the inadequacy of present representations of molecular structure. An excellent illustration of this inadequacy is the case of trimethylaluminum. Considerable evidence supported the veiw that the molecule is a dimer, but certain results appeared to be explicable only on the basis of a monomeric model. The issue was resolved only when these concepts of a static molecular framework were discarded in favor of a picture of the molecule as an intramolecular exchange system (4):



These examples serve to illustrate the fact that as the desire for increased comprehension of molecular structure grows, knowledge of the nature of exchange processes may well become of increasing concern.

Some molecules are extremely labile; others are virtually inert. For the purposes of studying the nature of the exchange process, systems are required in which exchange proceeds at a rate amenable to measurement of the desired quantities and in which structural species may be distinguished. For these reasons, the majority of data concerning this phenomenon have been obtained from investigation of the redistribution reactions of organo-metallic compounds.

The most generally accepted definition of an organometallic redistribution reaction is that proposed by Calingaert (5, 6) in the original work in this field. By this definition, a redistribution is a reaction of the type

$$R\text{-}M + Q\text{-}M' = Q\text{-}M + R\text{-}M'$$

where R is an alkyl or aryl group; Q is an alkyl, aryl, alkenyl, alkoxy, halogen, or hydrogen group; and M and M' are the same or different metal atoms. This original definition further stipulates that the distribution of products at equilibrium be that predicted solely by the laws of probability -- that is, random distribution.

In an earlier paper, Calingaert and Beatty (7) explain the mathematical formulation of random distribution for the general redistribution system, R_nM/R'_nM. The random equilibrium mixture will consist of the n+1 possible compounds, and their concentrations will be given by the corresponding terms in the binomial expansion of $(r_1 + r_2)^n$, where r_1 and r_2 are the initial mole fractions of R and R', respectively. Physically, this formulation indicates that the metal atom has no preference for one ligand over the other, and the equilibrium distribution of products corresponds to a perfect mixing of the ligands among the metal atoms.

In some systems, a more complicated definition of the random case is required. For example, Van Wazer, in his work with organosilicon compounds (8, 9, 10), encountered the problem of polymerization during redistribution. He therefore considered random sorting not only of the ligands, but also of the groups: R_4Si, R_3Si-, R_2Si-, $RSi-$, and $-Si-$, which he termed neso, end, middle, three-way branch, and four-way branch, respectively. Obviously, addition of these considerations greatly complicates the calculations. Fortunately, these refinements will not be needed in the systems chosen for this study. The definition of Calingaert and Beatty will be employed with the modification that redistribution need not lead to random equilibrium mixtures.

The thermodynamic implications of statistical redistribution may be discussed in the terminology of Leffler and Grunwald (11) who consider that the free energy of a molecule may be separated into three additive terms. For the species Q_nMR, where M-R is the bond of interest in exchange, the free energy (G) may be written as

$$G = G_{QnM} + G_{MR} + I_{QnM,MR}$$

The group free energy terms are assumed to be independent, and the I term represents an interaction between the two groups. This interaction term might encompass resonance interactions, steric effects, dipole interactions, effects on the hybridization of M, and other interactions. Because of the complexity of the interaction term, this factor can seldom be determined exactly.

When the interaction term equals zero, exchange of R for R' will result in a free energy change which is independent of the nature of Q_nM-. All enthalpy effects on the free energy will therefore cancel, and the overall free energy change will be that due to the entropy of mixing of the ligands R and R'. Since this entropy of mixing is the only driving force for exchange, the ligands will achieve random distribution among the metal atoms at equilibrium. When the interaction term is not equal to zero, this exchange will result in a free energy change which is no longer independent of the nature of Q_nM-, and the equilibrium distribution of products will no longer be random.

A somewhat different approach has been applied by Van Wazer and Moedritzer to the interpretation of their data on silicon systems (9). The equilibrium constant calculated statistically may be compared to that obtained experimentally as follows

$$\Delta G_{dev.\ from\ random} = \frac{-RT}{n} \ln \frac{K\ (exp)}{K(random)}$$

$$\Delta G_{dev} = \Delta H \text{ of formation of the mixed species from the end members}$$

Because this method of interpretating data is more amenable to the correlation of experimental data with system characteristics, it will be used in this thesis.

Of the many systems which have been studied, some have been reported to exhibit random redistribution, and others, nonrandom redistribution. Much of the earlier research centered on systems in which the exchanging ligands are relatively simple, and, as a result, most of the data show randomness (5, 6, 12). However, as early as 1919, Stock and Somieski reported (13) greater than random yields of product from the reactions

$$SiH_4 + SiH_2Cl_2 \longrightarrow 2\ SiH_3Cl$$

$$SiH_2Cl_2 + ZnMe_2 \longrightarrow SiH_2Me_2 + ZnCl_2$$

Similarly, the nonrandomness of redistribution in bis-organomercury/mercuric halide systems has been long known and employed in the preparation of organomercuric halides (14). Recent investigations have appended an interesting and unexplained note to this preparatory procedure. Apparently, these organometal halides, RMX, do not exist for any Group II metal other than mercury (15, 2). The great strides in preparatory organometallic chemistry in the past few years have made available for study many new systems in which the ligands differ considerably. Investigation of these more complex systems has produced a large body of data for both random and nonrandom cases. The work on silicon (8, 9, 10, 16, 17, 18, 19) and mercury systems (20, 21, 22, 23) is of particular interest in this thesis because the exchange times are of the magnitude necessary for easy study. Review articles and general references in which information on systems of other metals may be found are listed in the "Literature Cited" section of this thesis (24, 25, 26).

Despite the number and variety of systems which have been investigated, very little explanation has been offered for the fact that randomness is observed in certain cases but not in others. This study attempts to delineate the characteristics of the redistribution system which will predetermine the nature of the equilibrium distribution. For this purpose, systems were chosen for study in which the number of pertinent variables is a minimum.

The redistribution systems chosen for investigation were binary systems of various bisorganomercury compounds. Redistribution proceeds relatively slowly (days at the temperature employed) for mercury and silicon compounds. However, mercury systems offer two advantages over those of silicon: mercury compounds do not polymerize upon heating for prolonged times, and redistribution in the mercury systems leads to mixtures of three compounds as opposed to mixtures of five compounds for silicon systems. Both of these advantages for the mercury systems simplify the necessary statistical calculations, analytical procedures, and interpretation of data.

In the absence of side reactions, redistribution in these binary systems will result in equilibrium mixtures of three compounds

$$R_2Hg + R'_2Hg = 2\ RR'Hg$$

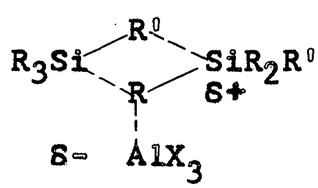
The statistical calculations of this case are quite simple. The random concentrations for each species are given by r^2, $2r(1-r)$, and $(1-r)^2$ for R_2Hg, $R'RHg$, and R'_2Hg, respectively, where r is the initial mole fraction (before redistribution) of ligand R (7).

The redistribution of many organometallic compounds, including those of mercury, have often been carried out in a variety of solvent media and with the aid of catalysts, which are usually metal halides or other Lewis acids. The catalytic effect of metal halides in redistribution was first reported by Calingaert (5, 6), and has since received considerable attention, notably by Russell (27). Calingaert believed that the halide reacts with the organometallic compounds, forming an intermediate organometal halide which then affects exchange by reaction with another organometallic molecule

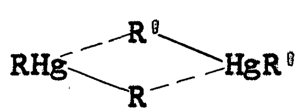
$$R_nM + AlX_3 \longrightarrow RAlX_2 + R_{n-1}MX$$

$$RAlX_2 + R'_nM \longrightarrow R'_{n-1}MR + R'AlX_2$$

Russell refuted this argument, however, and presented considerable evidence that the effect arises from polarization of the carbon-metal bonds through electron-deficient bond formation between the Lewis acid catalyst and the organometallic compound in the transition state. Russell's experimental results led him to the conclusion that the exchange involves a four-center transition state



Dessy has proposed a similar transition state for uncatalyzed mercury exchanges



An equally reasonable explanation based on the SE^2 mechanism has been proposed by Charman, Hughes, Ingold, and Thorpe (28).

Dessy states that the slow exchange times for mercury compounds may be explained as arising from the large size of the mercury atom which prevents the metal-metal approach necessary for exchange, or, alternatively, from the tendency of mercury to maintain 180° bond angles. Both factors would hinder formation of the three-center bonding orbitals of the four-center transition state (21). An additional factor which should be considered here is that bonds of small polarity, such as the carbon-mercury bond, tend to be relatively inert.

In accord with the concept of minimizing the pertinent variables and guarding against heterogeneous catalysis, the redistributions studied in this investigation were performed without catalysts or solvents (except in those cases where the two bisorganomercury compounds proved to be immiscible and therefore a solvent was employed to provide homogeneity). This procedure also presents the advantage that no possibility exists for the masking of ligand effects by ligand-catalyst interactions.

Dessy has suggested (29) that the factors which govern the nature of the equilibrium distribution should include the relative electronegativities, steric requirements, and resonance interaction capabilities of the exchanging ligands. This suggestion was used as a basis for the choice of systems for study in this work. Systems were chosen in which the exchanging ligands exhibit considerable difference in one of these properties and, as nearly as possible, equality in the others. In the case of electronegativity, this was done by studying redistribution in systems of a bisorganomercury compound and its perfluoro analog. Steric effects were investigated by using systems in which the exchanging ligands are geometrical isomers. The effect of different hybridization of the carbon orbitals was considered by employing alkyl, aryl, and alkenyl ligands. Some systems were also investigated in which more than one, or none, of the properties differ appreciably. In this manner, the additivity of effects was tested.

This particular approach is especially well adapted to the primary objectives of this study: the determination of the factors governing equilibrium distribution and the relative magnitudes of their effects, and the development of an ability to predict the degree of nonrandomness of the equilibrium state of a system from a knowledge of the initial components alone. Relative magnitudes of effects due to differing ligand characteristics determined in this manner can be considered strictly valid only for mercury systems and may be used for semi-quantitative predictions in uninvestigated mercury systems. However, at least the order of importance of the factors might be extendable to systems of other metals. These possible extensions are discussed in the "Interpretation of Results" section of this thesis.

The most convenient measure of randomness of equilibrium is the equilibrium constant; consequently, this quantity was calculated for each system investigated. From a tabulation of these values, equilibrium constants for uninvestigated mercury systems were predicted through construction of linear free energy relationships. The validity of this approach is discussed on the basis of the dependence of redistribution equilibria on ligand characteristics as determined in this study.

Because of the importance of ligand electronegativity in redistribution equilibria, as indicated by the results of the systems studied, the ligands studied may be arranged in an order of electronegativity on the basis of their effectiveness in causing nonrandomness of redistribution equilibria. These electronegativities may be compared to those proposed by Kharasch (30-34) on the basis of cleavage of organomercury compounds by HCl.

The results of this investigation provide a basis for the building of the knowledge necessary for a complete understanding of the ultimate questions of exchange in general and indicates a method by which this knowledge may be obtained. As more data become available, better predictions may be made and more general principles elucidated.

EXPERIMENTAL WORK

The experimental work required in this investigation consisted of the preparation and purification of materials, the performance of redistribution reactions, and the analysis of redistribution mixtures.

Preparation and Purification of Materials

All materials which are not listed below were commercial "reagent grade" materials which were used without further purification.

Solvents. Tetrahydrofuran (THF) for use in Grignard preparations was distilled from lithium aluminum hydride ($LiAlH_4$) before use. Tetrachloroethane used in the preparation of cyclopropyl bromide was distilled from phosphorus pentoxide (P_4O_{10}). Toluene was dried over sodium metal and distilled before use as a solvent in redistribution mixtures.

Reagents. Cyclopropyl bromide was prepared according to the method of Meek and Osuga (35) with the modification that the preparation was scaled up six times. Ethyl mercuric chloride and bromobenzene, reagent grade materials, were used without further purification.

Bisorganomercury Compounds. All bisorganomercury compounds were stored in brown bottles in a cold box (0°C.). Before each use of these compounds in redistribution experiments, the purity of each was checked by gas-liquid chromatography (GLC), and, when necessary, they were purified by vacuum distillation. The two exceptions to this procedure were the two solid compounds, bis(perfluoro-t-butyl)mercury, $(t\text{-}C_4F_9)_2Hg$, and diphenylmercury, $(C_6H_5)_2Hg$. Since these two compounds showed no tendency to decompose, they were used without further purification.

Bis(cyclopropyl)mercury, $(c\text{-}C_3H_5)_2Hg$, was prepared by the method of Reynolds, Dessy, and Jaffe (36) with the modifications that cyclopropyl bromide was added to the reaction flask as a solution of 0.19 mole cyclopropyl bromide in 50 ml THF, and the solution was allowed to reflux throughout addition.

Dimethylmercury, $(CH_3)_2Hg$, diethylmercury, $(C_2H_5)_2Hg$, and diphenylmercury, $(C_6H_5)_2Hg$, were purchased from Eastman Kodak, Rochester, New York; divinylmercury, $(C_2H_3)_2Hg$, was purchased from Orgmet, Hampstead, New Hampshire; bis(n-propyl)mercury, $(n\text{-}C_3H_7)_2Hg$, and bis(i-propyl)mercury, $(i\text{-}C_3H_7)_2Hg$, were purchased from K and K Laboratories, Plainview, New York;

bis(perfluoro-t-butyl)mercury, $(t\text{-}C_4F_9)_2Hg$, and bis(perfluoro-i-propyl)mercury, $(i\text{-}C_3F_7)_2Hg$, were donated by E. I. du Pont de Nemours and Company, Wilmington, Delaware. The preparation and physical constants of the perfluoro compounds have been reported by Aldrich (37), and those for the other compounds are recorded in Table 14 of the Appendix. These values were taken from "Handbook of Organometallic Compounds" (38).

Cyclopropylethylmercury, $(c\text{-}C_3H_5HgC_2H_5)$ was prepared in a manner analogous to the method of Hilpert and Gruttner for the preparation of unsymmetrical bisorganomercury compounds (39). In a 250-ml, 3-necked flask equipped with stirrer, reflux condenser, and dropping funnel and maintained under an atmosphere of dry nitrogen, 0.50 g magnesium turnings were just covered with THF. A solution of 2.50 g cyclopropyl bromide in 20 ml THF was placed in the dropping funnel, and approximately 5 ml of this solution were added to the flask. The reaction was initiated by heating to reflux for a few minutes. The heating mantle was then removed and the remainder of the solution was added at a rate to maintain refluxing. When addition was complete, the mixture was heated at reflux for an additional hour. A solution of 3.50 g ethylmercuric chloride, (C_2H_5HgCl), in 30 ml THF was then added dropwise to the flask. When all the C_2H_5HgCl had been added, the mixture was cooled and hydrolyzed with 30 ml H_2O. The organic layer was extracted with diethyl ether, washed with several portions of H_2O, and dried over $CaCl_2$. The solvent was removed at room temperature, using a water aspirator; the remaining liquid was transferred to a small distilling flask and vacuum distilled (boiling range 50-90°C./ 14 mm Hg). The distillation yielded 0.79 g of colorless liquid which, upon GLC analysis, was found to contain 7.3% $(C_2H_5)_2Hg$, 85.6% $c\text{-}C_3H_5HgC_2H_5$, and 7.1% $(c\text{-}C_3H_5)_2Hg$. Based on C_2H_5HgCl, the yield of $c\text{-}C_3H_5HgC_2H_5$ was 19% of theory.

Ethylphenylmercury ($C_2H_5HgC_6H_5$) was prepared by the procedure of Hilpert and Gruttner (38) with the modification that THF rather than diethyl ether was used as solvent.

Procedures for Redistribution Reactions

The redistribution reactions were carried out in a manner similar to that employed by Rausch (20); however, certain modifications of his procedure were required for some systems.

Dimethylmercury/Diethylmercury System. Appropriate quantities (0.05-0.30 g) of $(CH_3)_2Hg$ and $(C_2H_5)_2Hg$ were weighed into a small vial which had been flushed with dry nitrogen. The weights were recorded and used to calculate the initial mole fractions of the two reactants. Twenty-microliter (ul) aliquots of this mixture were then transferred to 1-ml glass vials which had been flushed with nitrogen. These vials were cooled under nitrogen in a Dry Ice-acetone bath and sealed. This procedure was repeated until six sets of samples of different initial molar ratios were prepared. The vials were completely submerged in an oil bath at 90 $\pm$ 2^{o}C. One vial of each set was removed from the bath every 24 hours and analyzed by GLC. This procedure was repeated until two subsequent analyses (difference in total reaction time of 24 hours) yielded the same relative concentrations of the three species to within experimental error (1%). Duplication of the values was taken as evidence of equilibrium. At least one vial was left in the bath for a longer time (about 200 hours) to provide a further check on the attainment of equilibrium. This procedure was applied to each of the six sets of samples and equilibrium values recorded for each.

Diethylmercury/Bis(cyclopropyl)mercury System. The same procedure as that above was followed except that five sets of samples were prepared. As a further check on the attainment of equilibrium in this system, the reverse reaction was studied. Twenty-ul aliquots of the prepared c-$C_3H_5HgC_2H_5$ sample were sealed into vials and heated in the bath. The same 24 hour analysis interval was employed, and duplication of the values was taken as evidence of equilibrium.

Diethylmercury/Divinylmercury System. The same procedure as that for the $(CH_3)_2Hg/(C_2H_5)_2Hg$ system was employed.

Divinylmercury/Bis(cyclopropyl)mercury System. The $(CH_3)_2Hg/(C_2H_5)_2Hg$ method was followed.

Divinylmercury/Diphenylmercury System. Appropriate amounts (0.05-0.10 g) of the two reactants were weighed into each reaction vial separately. Four vials of different molar ratios were prepared, and a fifth vial was prepared in which the molar ratio of one of the first four vials was duplicated. These vials were cooled under nitrogen in a Dry Ice-acetone bath and sealed. Then the vials were left in the oil bath for 100 hours. The first four samples were removed; the vials were opened; the contents were dissolved in CCl_4 and transferred to NMR tubes. The NMR spectra of each sample was recorded and the peaks were identified by comparison to the spectra of the pure compounds. The fifth sample was removed from the bath after 150 hours and analyzed by NMR to check the attainment of equilibrium.

Diethylmercury/Diphenylmercury System. The $(C_2H_3)_2Hg/(C_6H_5)_2Hg$ method was used. The attainment of equilibrium was also checked by study of the reverse reaction as was done in the $(C_2H_5)_2Hg/(c\text{-}C_3H_5)_2Hg$ system.

<u>Diethylmercury/Bis(n-propyl)mercury System</u>. The $(CH_3)_2Hg/(C_2H_5)_2Hg$ procedure was followed.

<u>Diethylmercury/Bis(i-propyl)mercury System</u>. The $(CH_3)_2Hg/(C_2H_5)_2Hg$ method was used.

<u>Bis(perfluoro-i-propyl)mercury/Bis(n-propyl)mercury System</u>. The immiscibility of these two compounds necessitated the use of a solvent. The $(CH_3)_2Hg/(C_2H_5)_2Hg$ method was employed with the modification that ½ ml of toluene was added to each sample to provide homogeneity. The validity of this modification was checked by repeating the reaction of the $(CH_3)_2Hg/(C_2H_5)_2Hg$ system in toluene solution.

<u>Bis(perfluoro-i-propyl)mercury/Bis(i-propyl)mercury System</u>. The $(i\text{-}C_3F_7)_2Hg/(n\text{-}C_3H_7)_2Hg$ method was followed.

<u>Bis(perfluoro-t-butyl)mercury/Bis(n-propyl)mercury System</u>. The $(i\text{-}C_3F_7)_2Hg/(n\text{-}C_3H_7)_2Hg$ procedure was followed; however, the two compounds were miscible with toluene at reaction temperature but not at room temperature.

<u>Bis(perfluoro-t-butyl)mercury/Bis(i-propyl)mercury System</u>. The $(i\text{-}C_3F_7)_2Hg/(n\text{-}C_3H_7)_2Hg$ method was employed.

Analysis of Redistribution Mixtures

The analyses required for the characterization of the redistribution systems included the quantitative analysis of the relative concentrations of the three species present in each mixture and the qualitative identification of the species to be associated with each concentration.

Quantitative Analyses. The relative concentrations of components of redistribution mixtures were determined either by NMR or GLC analysis. NMR analysis was used only for systems containing diphenylmercury, which could not be analyzed by GLC.

All GLC analyses were performed using a Perkin-Elmer Model 154 Vapor Fractometer equipped with a 2-meter, DC-200 silicon (2.5% by weight on Chromsorb W 80/100) column. The column temperatures and pressures used were different for each system. These conditions are noted on each of the sample chromatograms presented in the Appendix and are collected in Table 1 in the "Experimental Results" section.

The area under each GLC peak was taken as proportional to the concentration of the species responsible for the peak. Peak areas were determined by cutting out and weighing the peaks. Peak weight ratios were then considered as molar ratios for the respective compounds. Calibration of this technique indicated a reproducibility error of less than 1%. In those cases where two of the three peaks were not completely resolved, the combined peak area was apportioned to the two species involved from consideration of the initial molar ratio of the mixture and from the stoichiometry of the reaction.

NMR analyses were performed using a Varian Associates Model A-60 NMR Spectrometer. This method of analysis was employed only for those systems containing diphenylmercury, and quantitative results were obtained from consideration of only the resonances due to phenyl protons. Pure $(C_6H_5)_2Hg$ exhibits a single sharp resonance (-7.35 ppm from tetramethylsilane) of the ten equivalent phenyl protons. The redistribution mixtures exhibited two sharp phenyl proton resonances separated by 3 cycles/second. The downfield peak was shown to be due to diphenylmercury protons, and the other due to the five phenyl protons of the unsymmetrical species. This identification was accomplished by adding pure diphenylmercury to one of the mixtures at room temperature. The downfield peak was observed to increase in area while the other remained unchanged. The areas of the peaks were determined using an integrator and were used to calculate the relative concentrations of the two corresponding species. The peak area for the unsymmetrical component was doubled to account for the difference in number of phenyl protons per molecule. With this correction, the area ratios were set equal to molar ratios. The relative concentration of the third component was then determined by difference. Preliminary calibration with a mixture containing known amounts of $(C_2H_5)_2Hg$ and $(C_6H_5)_2Hg$ indicated that the quantitative accuracy to be expected was approximately within 3%. The accuracy of the integrator was also checked by cutting out and weighing the peaks; about the same degree of error was found. An example of the phenyl proton spectra obtained for the $(C_2H_5)_2Hg/(C_6H_5)_2Hg$ system is presented in the Appendix (Fig. 18, 19). The spectra for the $(C_2H_3)_2Hg/(C_6H_5)_2Hg$ system were essentially the same as that shown.

Qualitative Analyses. Components of redistribution mixtures were identified on the basis of their infra-red (IR) spectra, NMR spectra, or GLC chromatograms. When GLC analysis was used to obtain quantitative results, the components were identified either by comparison of GLC retention time and peak shape to those for the pure substances (when these were available) or on the basis of their IR spectra. IR samples were obtained directly from the fractometer; as the component of interest was eluted from the column, the exit gases were condensed and collected. The IR spectra of these samples were then recorded using a Perkin-Elmer Model 521 IR Spectrophotometer. All samples were analyzed in the form of pure (neat) liquids in liquid microcells by the single-beam technique. Identification was achieved by matching the spectra with those of the pure compound (either with spectra obtained from pure samples prepared in this work or with spectra reported in the literature).

EXPERIMENTAL RESULTS

The experimental results of this study consist of data from identification of components of redistribution mixtures and from determination of the relative concentrations of the components.

Qualitative Results

The methods of separation and characterization of components of redistribution mixtures are outlined in the data which follow.

The wide variation in boiling points of the compounds which were studied required that different experimental conditions be employed for analysis of each system. Preliminary experimentation indicated the optimal conditions for each system and these conditions were employed for all analyses of that system. These conditions are recorded in Table 1. The retention times are characteristic of the components and were used as a basis for species identification. An example

Table 1. GLC Analysis Conditions*

System Components	Temperature (°C.)	Pressure (psig)	Flow Rate (ml/min)	Retention Time (min)
$(CH_3)_2Hg$ $C_2H_5HgCH_3$ $(C_2H_5)_2Hg$	75	6	250	2 4 9
$(C_2H_5)_2Hg$ $c\text{-}C_3H_5HgC_2H_5$ $(c\text{-}C_3H_5)_2Hg$	110	15	450	2 6 16
$(C_2H_3)_2Hg$ $C_2H_3HgC_2H_5$ $(C_2H_5)_2Hg$	80	6	300	2 6 7
$(C_2H_3)_2Hg$ $c\text{-}C_3H_5HgC_2H_5$ $(c\text{-}C_3H_5)_2Hg$	110	15	450	1 -- 16
$(C_2H_5)_2Hg$ $n\text{-}C_3H_7HgC_2H_5$ $(n\text{-}C_3H_7)_2Hg$	60	22	600	4 8 13
$(C_2H_5)_2Hg$ $i\text{-}C_3H_7HgC_2H_5$ $(i\text{-}C_3H_7)_2Hg$	60	22	600	4 8 15
$(i\text{-}C_3F_7)_2Hg$ $n\text{-}C_3H_7Hg(i\text{-}C_3F_7)$ $(n\text{-}C_3H_7)_2Hg$	70	15	500	1 2 8
$(i\text{-}C_3F_7)_2Hg$ $i\text{-}C_3H_7Hg(i\text{-}C_3F_7)$ $(i\text{-}C_3H_7)_2Hg$	70	15	500	1 2 9

* All GLC analyses were performed at constant column temperature using helium as the carrier gas.

chromatogram for each system in which this method of analysis was used is reproduced in the Appendix (Fig. 12-21).

The use of IR and NMR spectral techniques has been discussed in the preceding section.

Quantitative Results

The relative concentrations of the three components in each redistribution mixture were determined and average equilibrium constants and free energy deviations were then calculated from these data.

Concentration Data. The relative concentrations of mixture components are tabulated as molar percentages in the Appendix (Tables 4-13). The molar percentages have been plotted versus the initial molar composition for each system to facilitate comparison to the random case (Fig. 1-9). The graphs contain both the experimental results (solid lines) and the statistically calculated values (dashed lines).

Equilibrium Constants and Free Energy Deviations. For each set of concentrations, the equilibrium constant was calculated as

$$K = \frac{(\text{mole \% } RR'Hg)^2}{(\text{mole \% } R_2Hg)(\text{mole \% } R'_2Hg)}$$

These values were the averaged for all the mixtures of the system. The equilibrium constants reported are for 90°C., although analyses were performed at a variety of temperatures.

Because quenching and analysis times were negligible compared to total reaction time, significant changes in equilibrium during analysis were neglected. Free energy deviations from randomness were calculated from the average equilibrium constant in the manner explained in the "Introduction." These quantities are recorded in Table 2.

FIGURE 1. REDISTRIBUTION IN THE DIMETHYLMERCURY/DIETHYLMERCURY SYSTEM

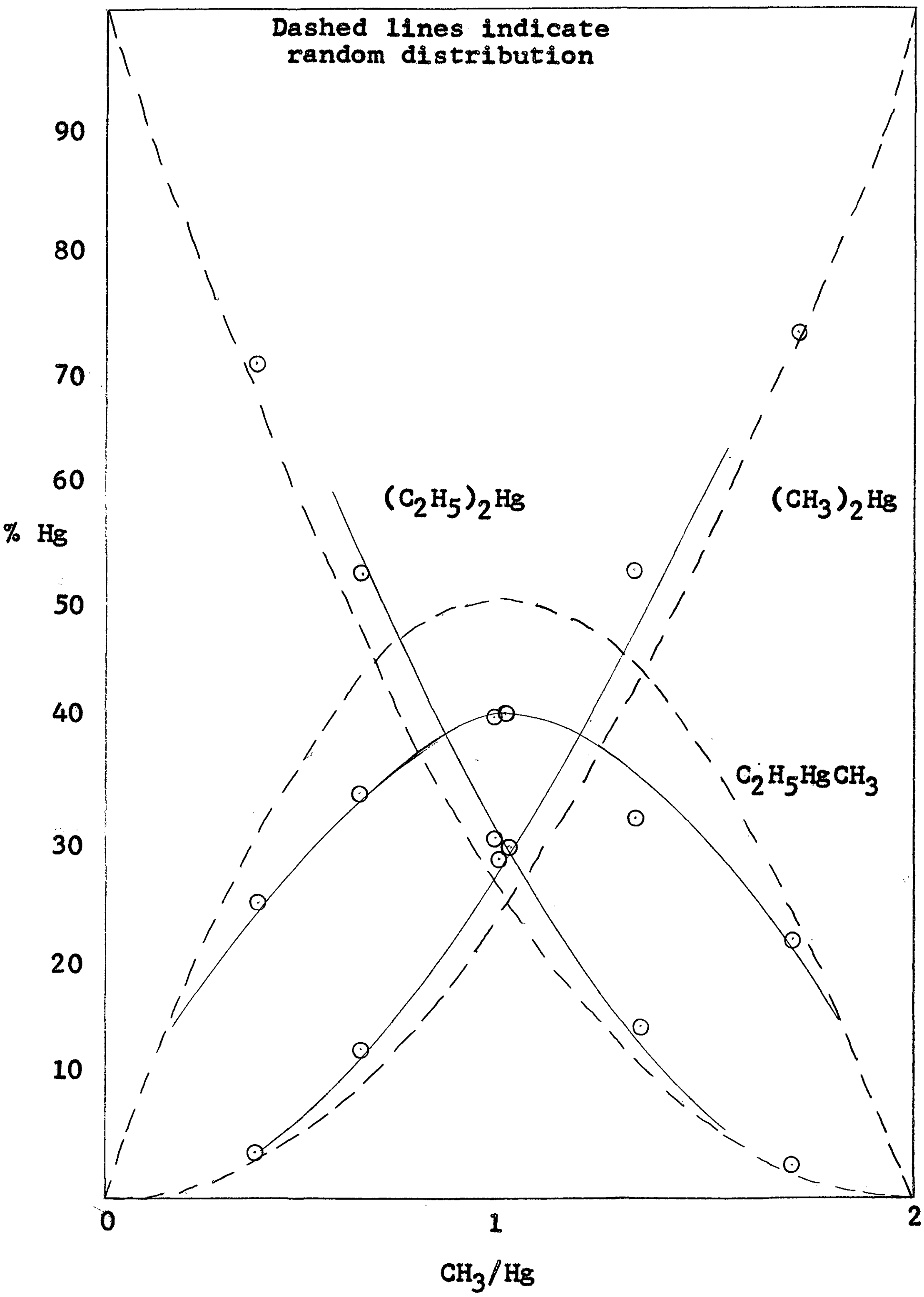


FIGURE 2. REDISTRIBUTION IN THE DIETHYLMERCURY/DICYCLOPROPYLMERCURY SYSTEM

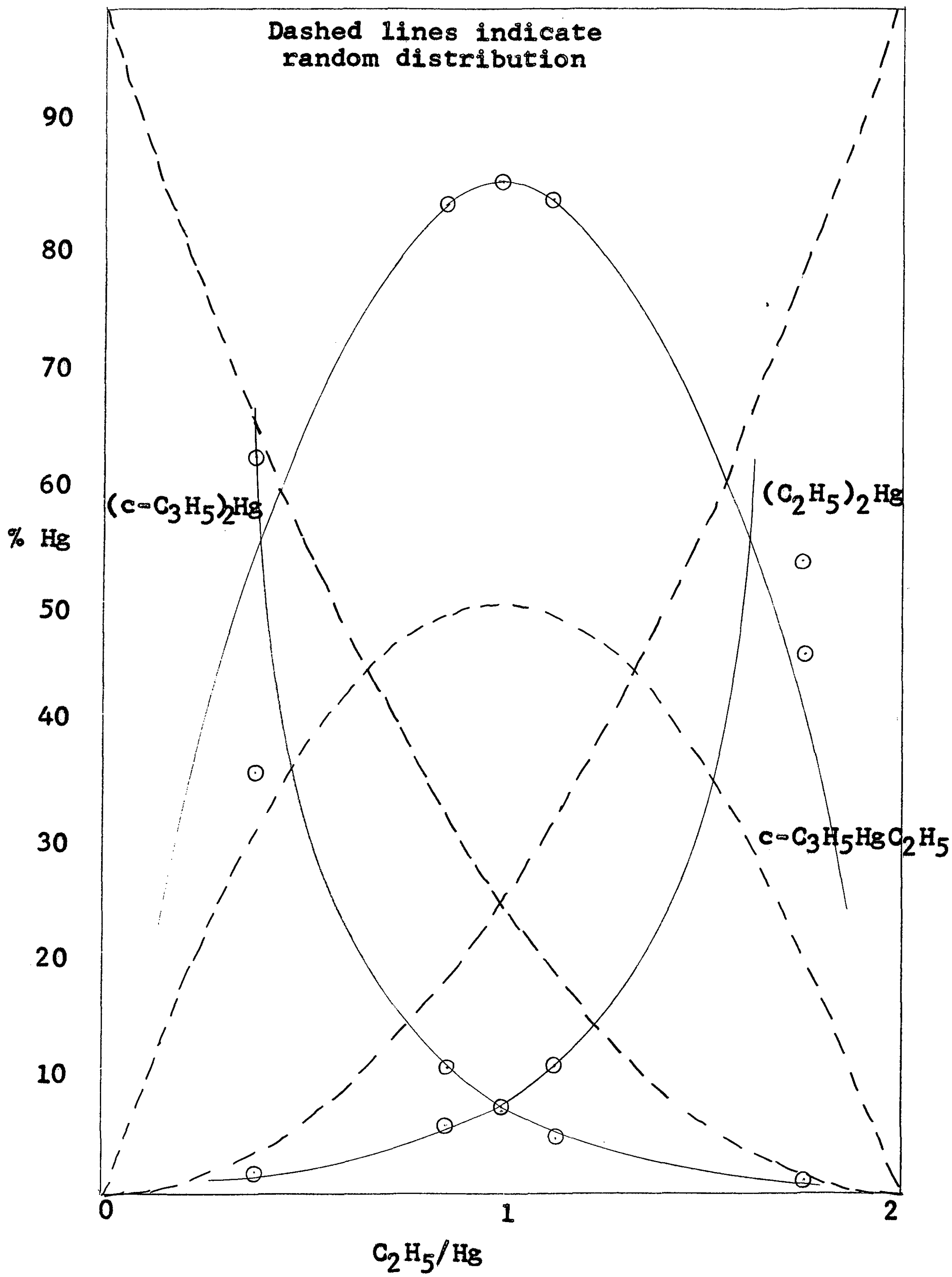


FIGURE 3. REDISTRIBUTION IN THE DIETHYLMERCURY/DIVINYLMERCURY SYSTEM

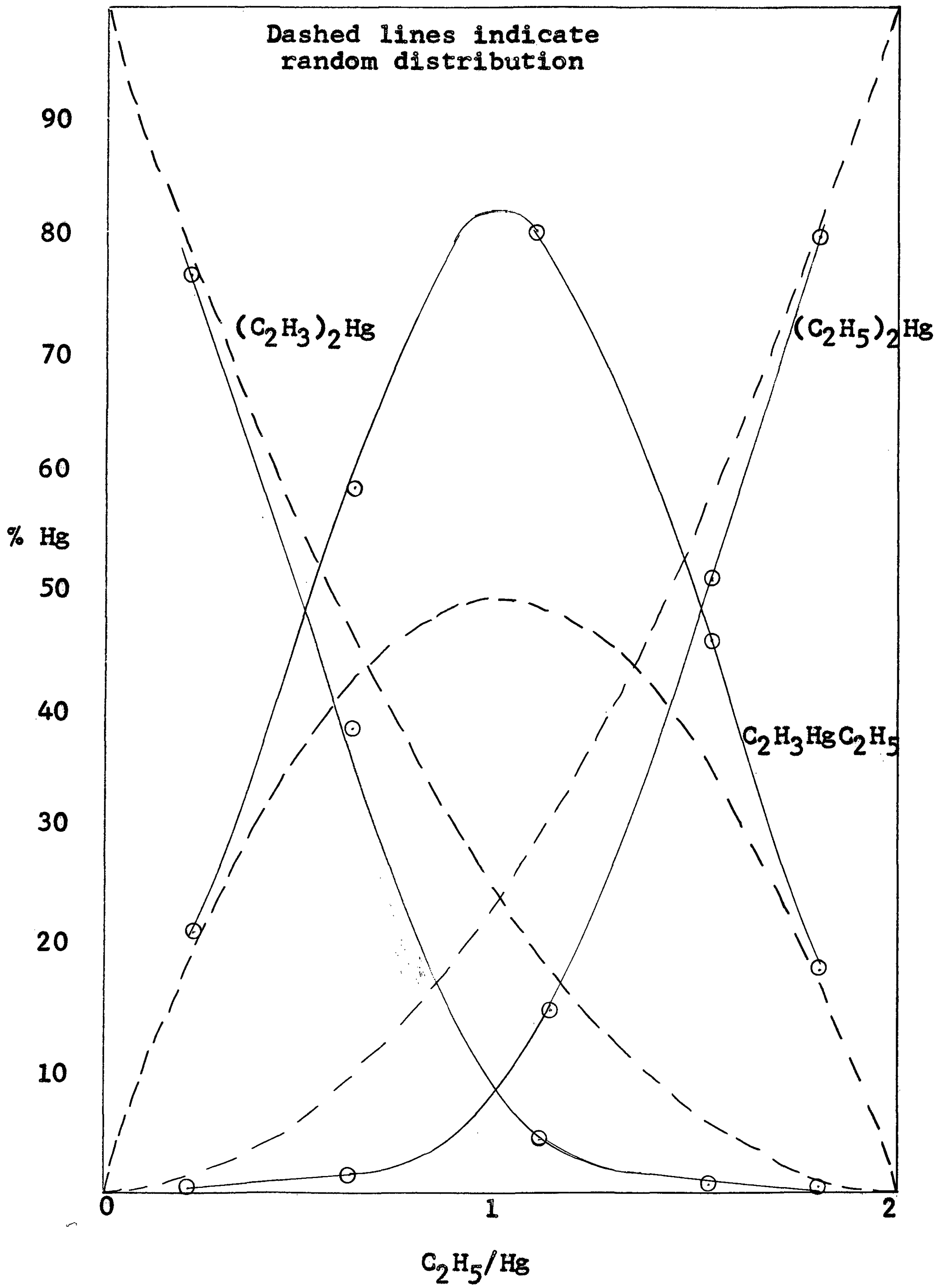


FIGURE 4. REDISTRIBUTION IN THE DIETHYLMERCURY/DIPHENYLMERCURY SYSTEM

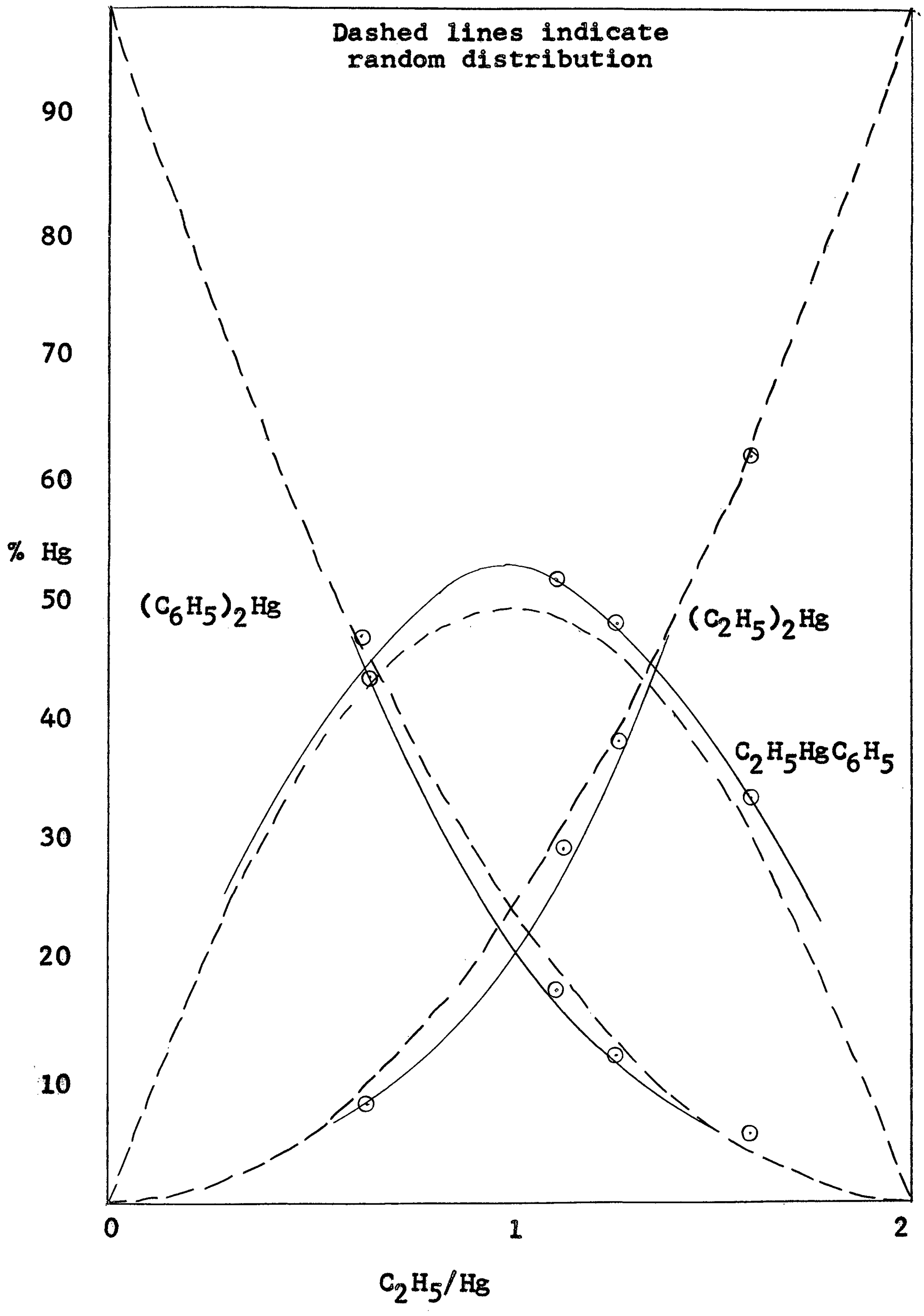


FIGURE 5. REDISTRIBUTION IN THE DIVINYLMERCURY/DIPHENYLMERCURY SYSTEM

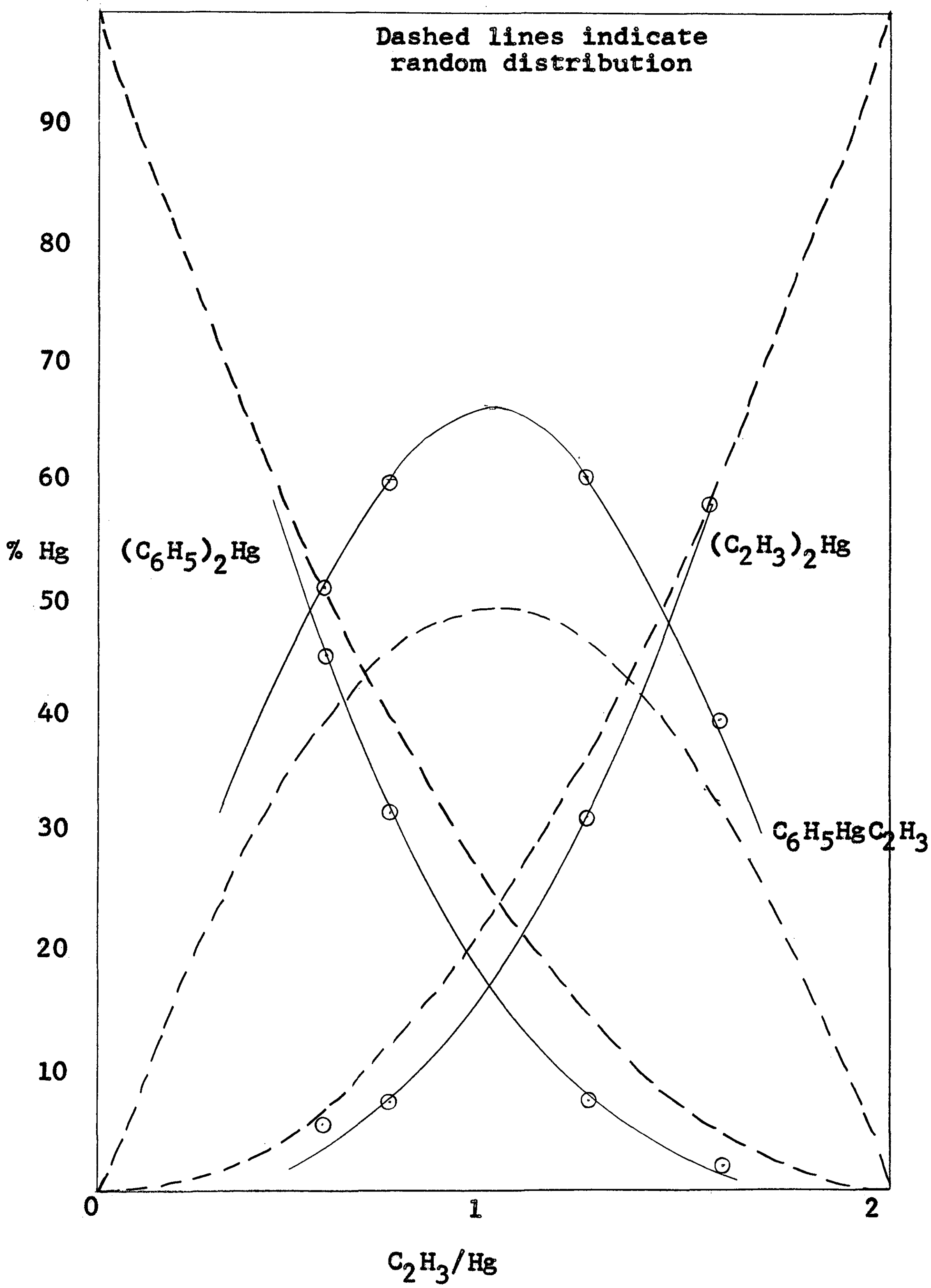


FIGURE 6. REDISTRIBUTION IN THE DIETHYLMERCURY/DI-n-PROPYLMERCURY SYSTEM

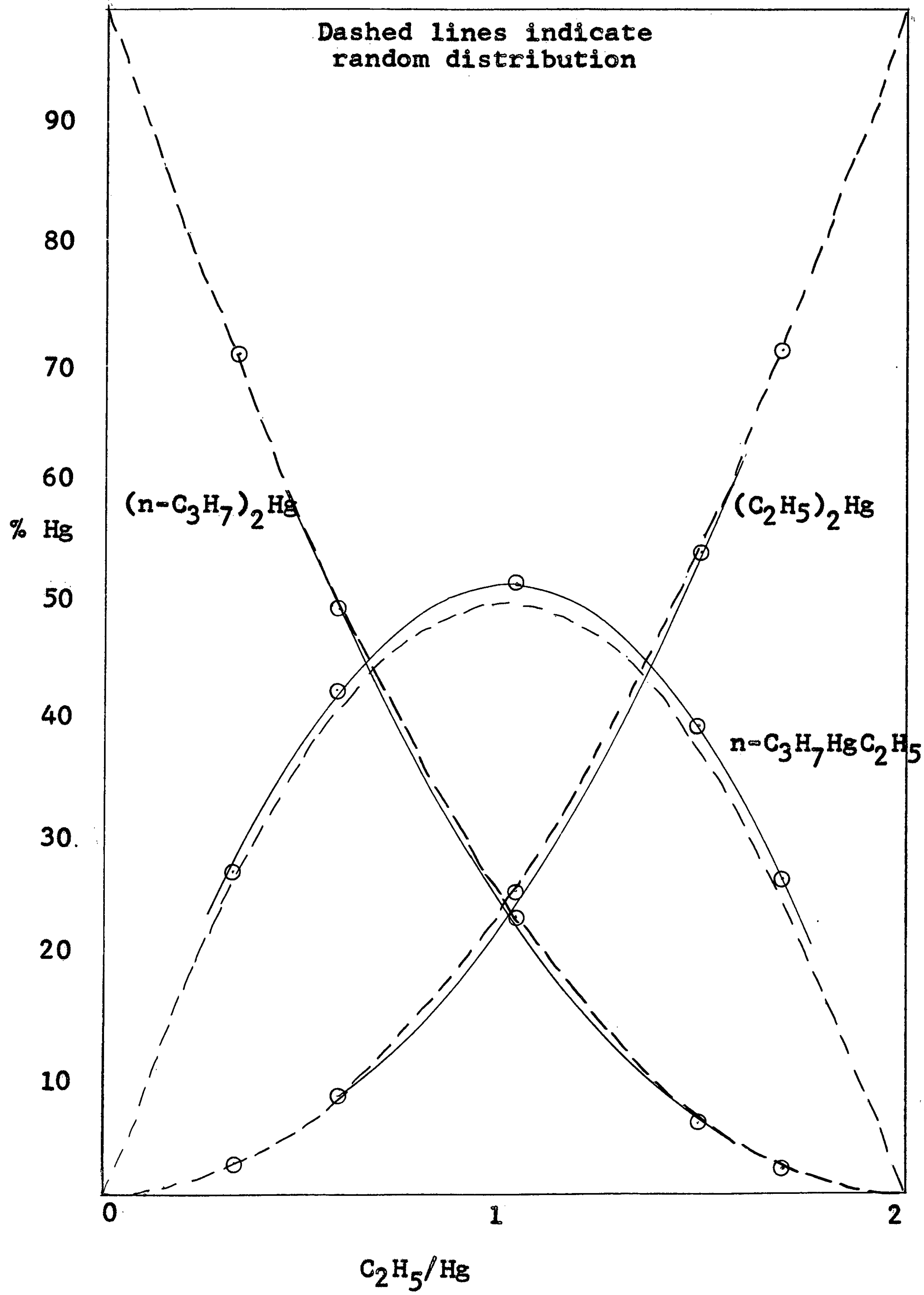


FIGURE 7. REDISTRIBUTION IN THE DIETHYLMERCURY/DI-i-PROPYLMERCURY SYSTEM

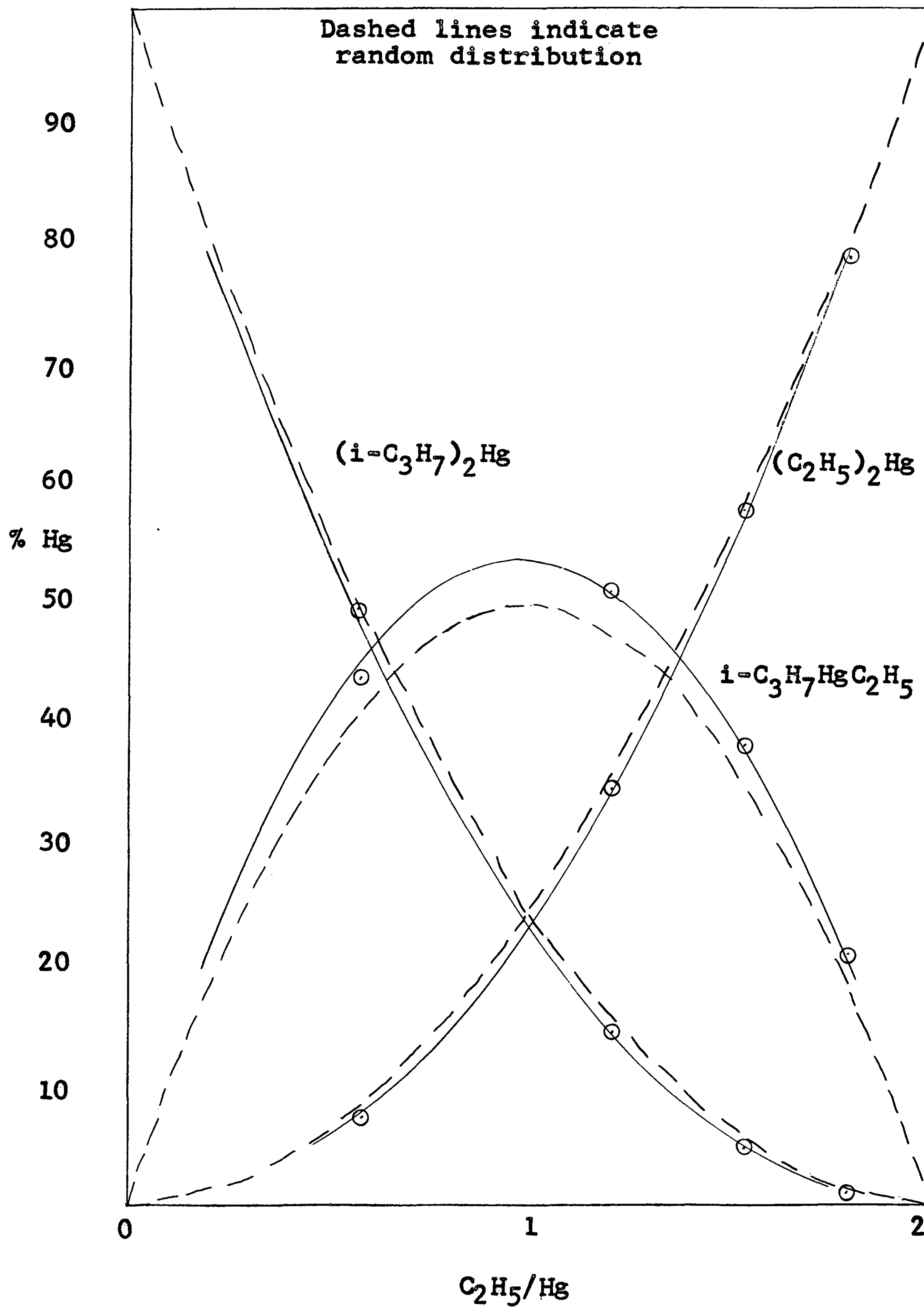


FIGURE 8. REDISTRIBUTION IN THE
BIS-PERFLUORO-i-PROPYLMERCURY/DI-n-PROPYLMERCURY SYSTEM

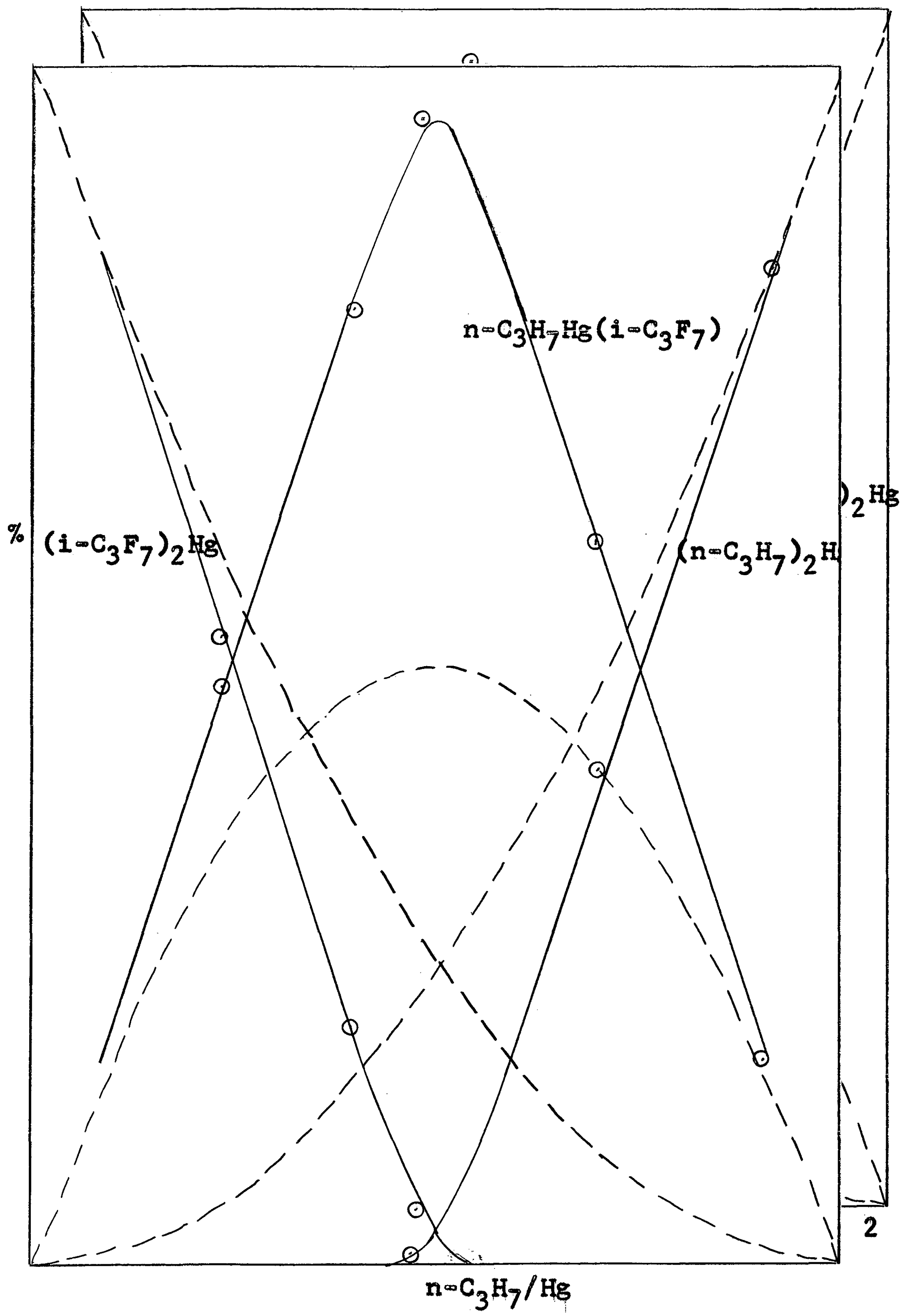


FIGURE 9. REDISTRIBUTION IN THE BIS-PERFLUORO-i-PROPYLMERCURY/DI-i-PROPYLMERCURY SYSTEM

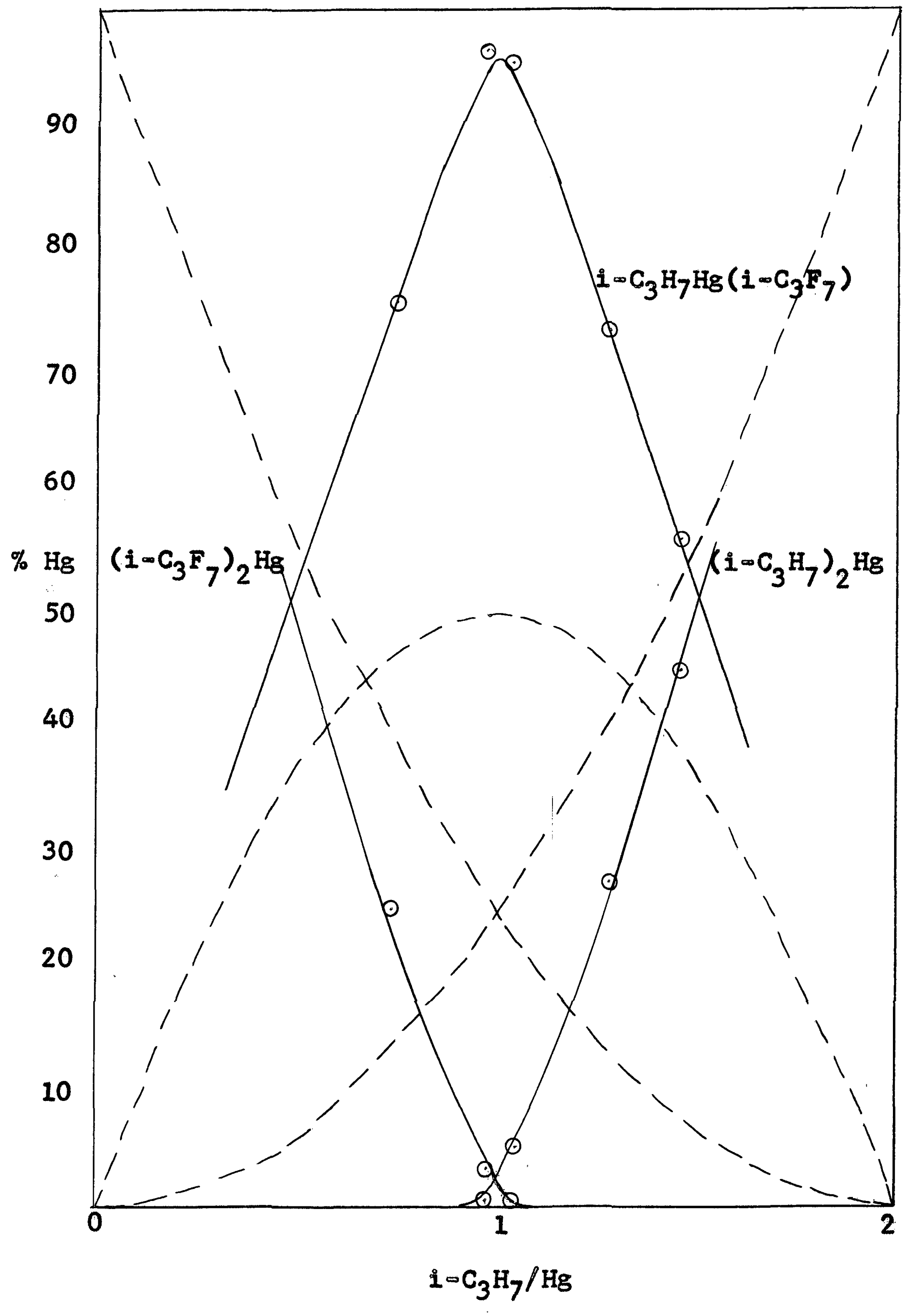


Table 2. Equilibrium Constants and Free Energy Deviations

System	K_{exp}	$\triangle F_{dev}$ (kcal/mole)
$(CH_3)_2Hg/(C_2H_5)_2Hg$	1.8	+ 0.6
$(C_2H_5)_2Hg/(c\text{-}C_3H_5)_2Hg$	100	- 2.3
$(C_2H_5)_2Hg/(C_2H_3)_2Hg$	100	- 2.3
$(C_2H_3)_2Hg/(c\text{-}C_3H_5)_2Hg$*	---	---
$(C_2H_5)_2Hg/(C_6H_5)_2Hg$	5.0	- 0.2
$(C_2H_3)_2Hg/(C_6H_5)_2Hg$	15.5	- 1.0
$(C_2H_5)_2Hg/(n\text{-}C_3H_7)_2Hg$	4.4	- 0.1
$(C_2H_5)_2Hg/(i\text{-}C_3H_7)_2Hg$	5.3	- 0.2
$(i\text{-}C_3F_7)_2Hg/(n\text{-}C_3H_7)_2Hg$	10^3	- 4
$(i\text{-}C_3F_7)_2Hg/(i\text{-}C_3H_7)_2Hg$	10^3	- 4
$(t\text{-}C_4F_9)_2Hg/(n\text{-}C_3H_7)_2Hg$**	---	---
$(t\text{-}C_4F_9)_2Hg/(i\text{-}C_3H_7)_2Hg$**	---	---

* Under conditions employed for reaction in this work, no reaction was observed in this system.

** No solvent could be found in which all components of these systems were completely miscible at room temperature. Therefore accurate GLC analysis was not possible; however, large equilibrium constants were indicated.

INTERPRETATION OF RESULTS

The relative importance of the various ligand characteristics in determining the position of redistribution equilibria may be determined by examining the results as presented in Table 2.

The role of the relative steric requirements of the exchanging ligands is illustrated by the results in the systems: diethylmercury/bis(n-propyl)mercury and diethylmercury/bis-(i-propyl)mercury. The n-propyl and i-propyl ligands may be considered to exhibit no significant difference in electronegativity, resonance interaction capability, or hybridization of the carbon orbitals. Differences in the equilibria in these two exchanges may then be attributed entirely to differences in steric requirements. The small difference in equilibrium constants (4.4 and 5.3) corresponds to a free energy difference of only approximately 0.1 kcal/mole. The relative steric requirements of the exchanging ligands therefore exert only minor influence on redistribution equilibria.

However, these two ligands do not differ greatly in steric requirements. When the exchanging ligands differ more in steric requirements (size) greater free energy differences are to be expected. For the ligands studied in this work, differences should be no more than twice that for n-propyl and i-propyl ligands. Then free energy deviations greater than 0.2 kcal/mole must, on the basis of this assumption, be attributed to effects other than purely steric requirements. This conclusion is reinforced by the fact that the equilibrium constants for redistribution in the bis(i-propyl)mercury/bis-(perfluoro-i-propyl)mercury and bis(n-propyl)mercury/bis-(perfluoro-i-propyl)mercury systems are indistinguishable to within the accuracy of analysis. However, the large degree of nonrandomness in these systems makes the interpretation less convincing.

This large degree of nonrandomness in the bis(perfluoro-i-propyl)mercury/bis(i-propyl)mercury system does, however, demonstrate well the effect of ligand electronegativity. The exchanging ligands in this system differ only in that the hydrogens of the i-propyl ligand have been replaced by fluorines in the perfluoro compound. Despite the slightly increased size of the fluorine atom as compared with that of hydrogen, these two ligands may reasonably be considered to differ significantly only in their relative electronegativities.

The nonrandomness of redistribution in this system may therefore be attributed entirely to the electronegativity effect. Obviously, the relative electronegativities of the exchanging ligands exerts a major influence on redistribution equilibria. This influence of electronegativity is further demonstrated by the results for the bis(perfluor-i-propyl)mercury/bis-(n-propyl)mercury system and by the results of Rausch (20) for the dimethylmercury/bis(perfluorophenyl)mercury system ($K > 2 \times 10^3$).

The n-propyl, vinyl, cyclopropyl, and phenyl ligands have different hybridizations of the ligand carbon orbitals. These ligands also differ in steric requirements, resonance interaction capabilities, and electronegativity. As stated previously, effects due to steric differences will be assumed to result in free energy differences no greater than 0.2 kcal/mole. The presence of pi systems in the phenyl and vinyl ligands suggests the possibility of resonance interaction between the filled orbitals of mercury and the vacant pi antibonding orbitals of the ligands. This "back-donation" decreases electron density build-up on the mercury and thereby stabilizes the compound. When both ligands contribute to this stabilization, redistribution with saturated ligands, which are incapable of such interaction, would be expected to be unfavorable. Carbon atoms having sp, sp^2, and sp^3 hybridization are known to differ somewhat in electronegativity; therefore, effects due to differences in orbital hybridization might best be considered a special case of effects due to electronegativity rather than a separate, isolated phenomenon.

Because of the multiplicity of differences in these ligands, differences in equilibria for exchanges of these ligands with the ethyl ligand cannot be unequivocally explained as arising from orbital hybridization effects. Despite these difficulties, the randomness of the ethyl/n-propyl exchange and the nonrandomness of the ethyl/vinyl and ethyl/cyclopropyl exchanges does indicate some influence of carbon orbital hybridization on the equilibria. As stated previously, steric differences cannot be credited with effects of this magnitude, and resonance effects would favor decreased formation of the unsymmetrical species. The nonrandomness must then be attributed to orbital hybridization effects which, as previously stated, may be considered a special case of electronegativity effects.

The results for the diethylmercury/diphenylmercury system appear irregular in this series. The steric and hybridization differences between the ethyl and phenyl ligands suggest that this exchange should be more nonrandom than is observed. This decrease in nonrandomness may be considered to arise from stabilization of the diphenylmercury by resonance interaction. The mechanism of this stabilization has been discussed above. Why this resonance effect does not apparently operate to a comparable extent in the vinyl/ethyl exchange remains to be explained.

Within the framework of the assumptions made above, both resonance interaction capabilities and carbon orbital hybridizations may be considered to be of importance in determining the nonrandomness of redistribution equilibria. From the data, the two effects appear to be of comparable magnitude. The order of relative importance of the ligand characteristics, from the above discussion, is as follows: electronegativity, resonance interaction capabilities and carbon orbital hybridization, and steric requirements.

If, as suggested above, steric requirements and resonance interaction capabilities do not play major roles in ethyl/vinyl and ethyl/cyclopropyl exchanges, then the results for these two exchanges may be interrupted to indicate that the vinyl and cyclopropyl ligands are of comparable electronegativity. On this basis, the predicted value for the equilibrium constant for vinyl/cyclopropyl exchange would be 4. Experimentally, this exchange was not observed to occur within reasonable reaction times. An explanation of the lack of observed reaction in this system is not immediately obvious.

The presence of catalytic amounts of mercuric halides has been suggested (29) as a necessary requirement for all mercury exchanges. However, mass spectral analysis of samples of the diethylmercury, divinylmercury, and bis(cyclopropyl)-mercury used in this work demonstrated the absence of halides within the limits of detectability of the instrument (approximately 1 part per million). The lack of reaction may be due to high free energy of activation for the exchange (kinetic control) or to instability of vinylcyclopropyl-mercury (thermodynamic control). The data are insufficient to justify resolution of this question.

The prediction of equilibrium constants in uninvestigated systems might be approached in a variety of ways; however, because the equilibrium constant has been considered to depend only on ligand characteristics, the possibility of construction of a linear free energy relationship is suggested. Because steric effects have been shown to be of minor importance, the free energy deviation in redistribution may be considered a function of electronegativity, orbital hybridization (which may also be basically an electronegativity effect), and resonance interaction characteristics of the ligands. These three factors effectively measure the nature of electron density distribution in the molecule. Therefore, these systems appear ideally suited for the linear free energy treatment.

The free energy deviations recorded in Table 2 may be used to construct the relationship; however, writing the deviations in terms of equilibrium constants will be more convenient for the purpose of prediction:

$$\ln \frac{K\,(R/R')}{K_{random}} = a \ln \frac{K\,(R''/R')}{K_{random}}$$

In this expression, K (R/R') represents the equilibrium constant for the bisorganomercury system in which the exchanging ligands are R and R', and K_{random} represents the statistical equilibrium constant for the same system. This quantity is set equal to a constant times the corresponding quantity for the exchange of R'' with the same ligand, R'. The constant, "a", is then characteristic of the differences between R and R'' and is assumed independent of R'. Then, by varying R' and utilizing the constant value of "a", the equilibrium constant for R''/Q exchange may be predicted from the known equilibrium constant for R/Q exchange.

Fron Table 2, the following equation may be written:

$$\frac{\ln K(C_2H_5/C_2H_3)}{4} = aC_6H_5 \quad \frac{\ln K(C_6H_5/C_2H_3)}{4}$$

$$aC_6H_5 = \frac{\ln\,(100/4)}{\ln\,(15/4)} = 2.4$$

This value of aC_6H_5 may now be used to predict equilibrium constants in other phenyl exchanges when the equilibrium constant of the corresponding ethyl exchange is known. For example:

$$\ln \frac{K\ (C_2H_5/n\text{-}C_3H_7}{4} = a_{C_6H_5} \ln \frac{K\ (C_6H_5/n\text{-}C_3H_7)}{4}$$

$$K\ (C_6H_5/n\text{-}C_3H_7) = 4.5$$

In this manner, the equilibrium constants may be predicted for phenyl exchange with all the ligands for which exchange with ethyl was studied. These predicted K values may then be used to calculate "a" values for the other ligands (with respect to ethyl). These "a" values may in turn be used to predict other equilibrium constants.

$$a_{Vi} = \ln \frac{K\ (C_2H_5/C_6H_5)}{4} \div \ln \frac{K\ (C_2H_3/C_6H_5)}{4} = 0.16$$

The "a" values for each ligand and the equilibrium constants predicated using these values are recorded in Table 3.

Time did not permit collection of data sufficient to check the validity of the equilibrium constants predicted in this way. Therefore, little more can be said about this interpretation except that equilibrium constants may be predicted on the basis of differences in ligand characteristics that have been shown to be pertinent in determining these values. As more data become available in the literature, the predicted equilibrium constants may be checked, and hence

Table 3. Predicted Equilibrium Constants

Ligand	"a" Value
C_6H_5	2.4
$n-C_3H_7$	2.1
$i-C_3H_7$	4.6
C_2H_3	0.16
$c-C_3H_5$	0.16

System	Equilibrium Constant
$(C_6H_5)_2Hg/(n-C_3H_7)_2Hg$	4.5
$(C_6H_5)_2Hg/(i-C_3H_7)_2Hg$	4.2
$(C_6H_5)_2Hg/(c-C_3H_5)_2Hg$	16
$(C_2H_3)_2Hg/(n-C_3H_7)_2Hg$	22
$(C_2H_3)_2Hg/(i-C_3H_7)_2Hg$	7.3
$(c-C_3H_5)_2Hg/(n-C_3H_7)_2Hg$	22
$(c-C_3H_5)_2Hg/(i-C_3H_7)_2Hg$	7.3
$(i-C_3H_7)_2Hg/(n-C_3H_7)_2Hg$	4.2

the validity of the interpretations presented here may be tested.

Because of the assumptions that the linear free energy relationship depends only upon differences in the ligands, the "a" values calculated here should be independent of the metal. Therefore, this method of equilibrium constant prediction offers possibilities for predictions for a wide variety of systems. Certain precautions must be taken, however. The statistical equilibrium constant used in the relationship is 4 in all mercury systems studied; however, as indicated in the "Introduction", this quantity varies in various systems.

In all the extensions to systems of other metals which have been mentioned above, it should be realized that as the polarity of the carbon-metal bond becomes greater, small ligand differences may be expected to represent smaller effects on total polarity. However, because the linear free energy relationship correlates only systems of the same metal, this disadvantage would seem to be minimized. Another constant may be included in the expression to adjust the "a" values for the susceptibility of the metal in question to ligand properties. Even the order of importance of ligand effects should be used with caution in systems where the metal is considerably more electropositive than mercury.

Although the results of this study have not provided unequivocal predictions of redistribution equilibria or a comprehensive explanation of these phenomena, they have defined controlling factors and offer a method of predictions based on these factors.

APPENDIX

FIGURE 10. $(CH_3)_2Hg/(C_2H_5)_2Hg$

GAS-LIQUID CHROMATOGRAMS OF SYSTEM

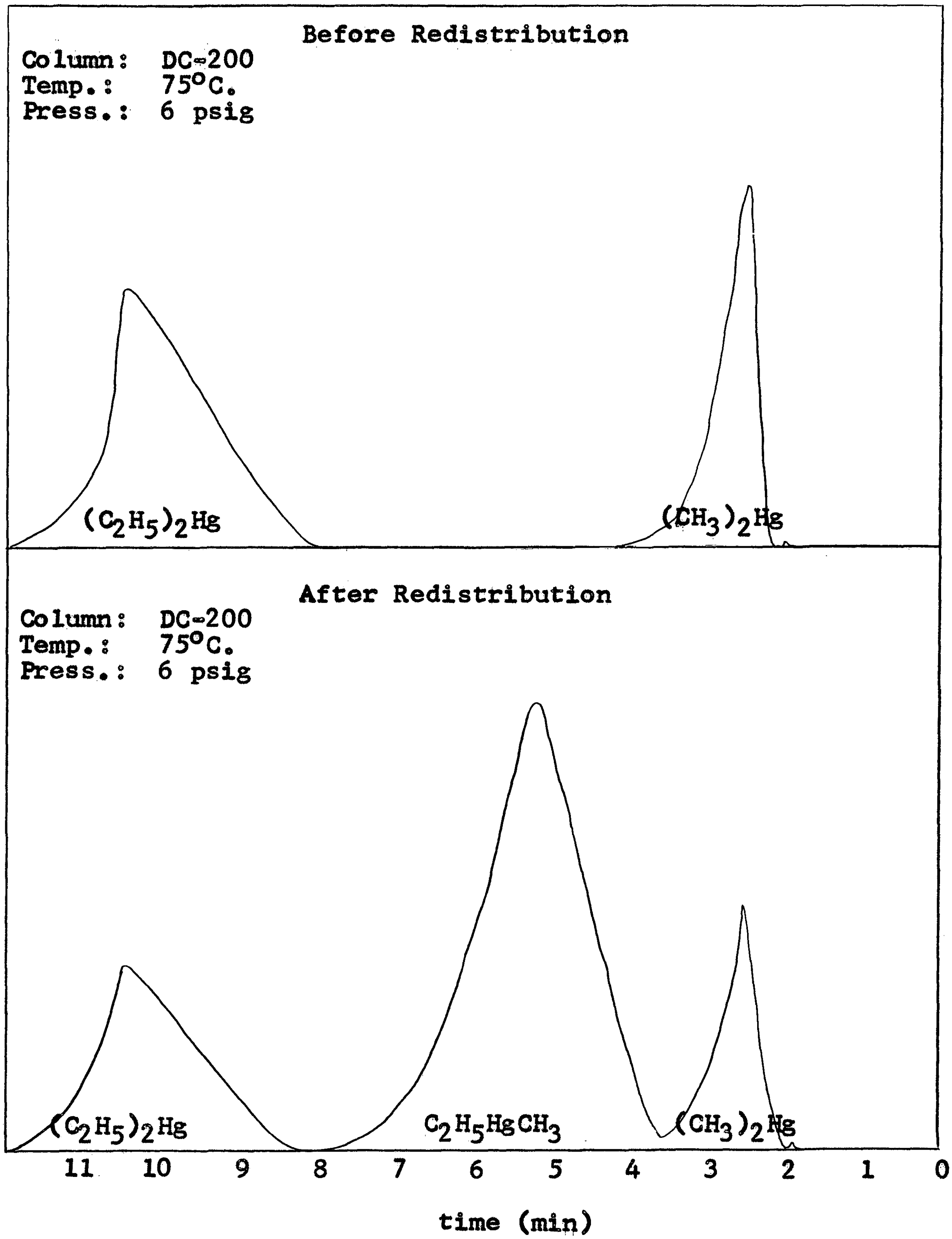


FIGURE 11. $(C_2H_5)_2Hg/(c\text{-}C_3H_5)_2Hg$

GAS-LIQUID CHROMATOGRAMS OF SYSTEM

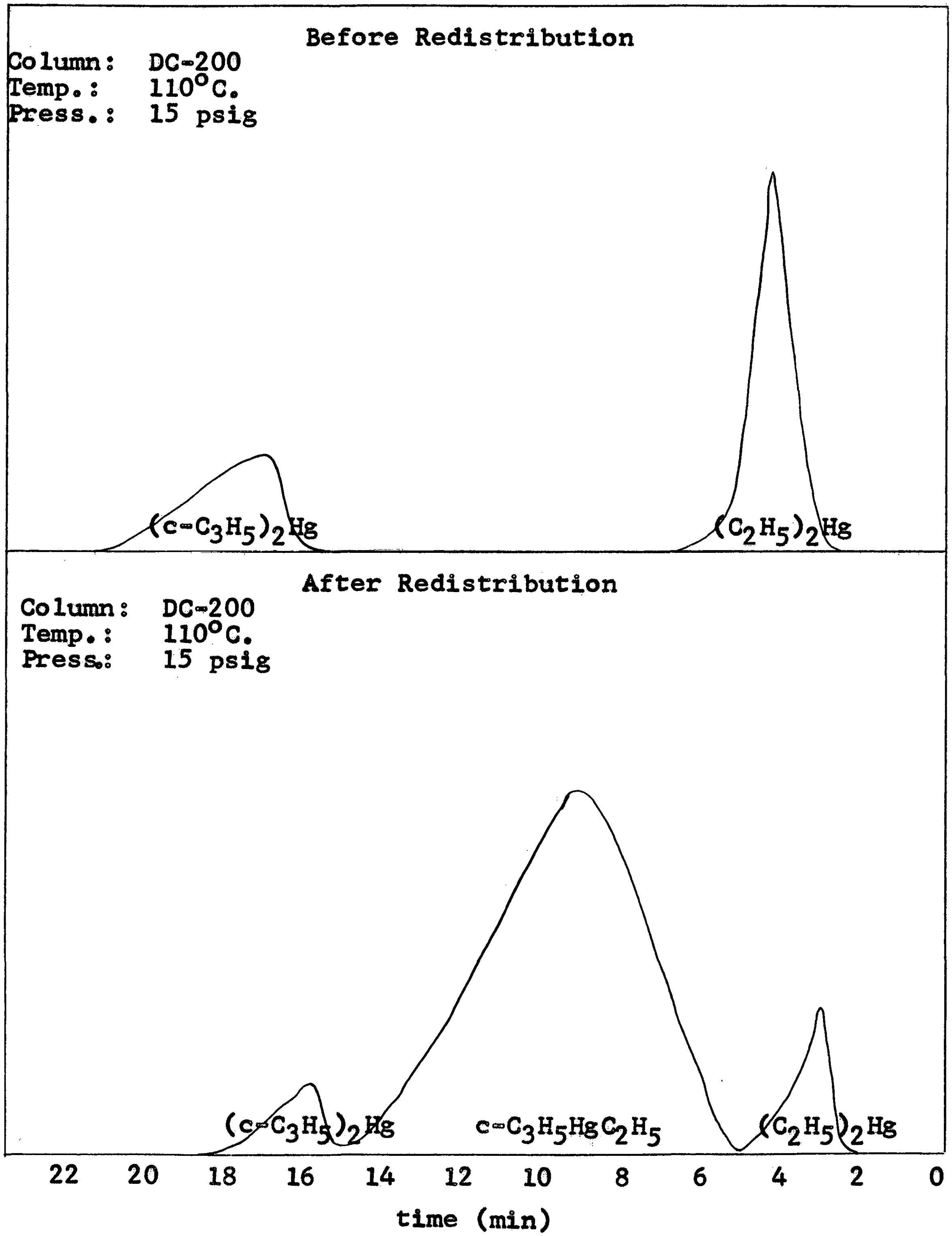


FIGURE 12. $(C_2H_5)_2Hg/(C_2H_3)_2Hg$

GAS-LIQUID CHROMATOGRAMS OF SYSTEM

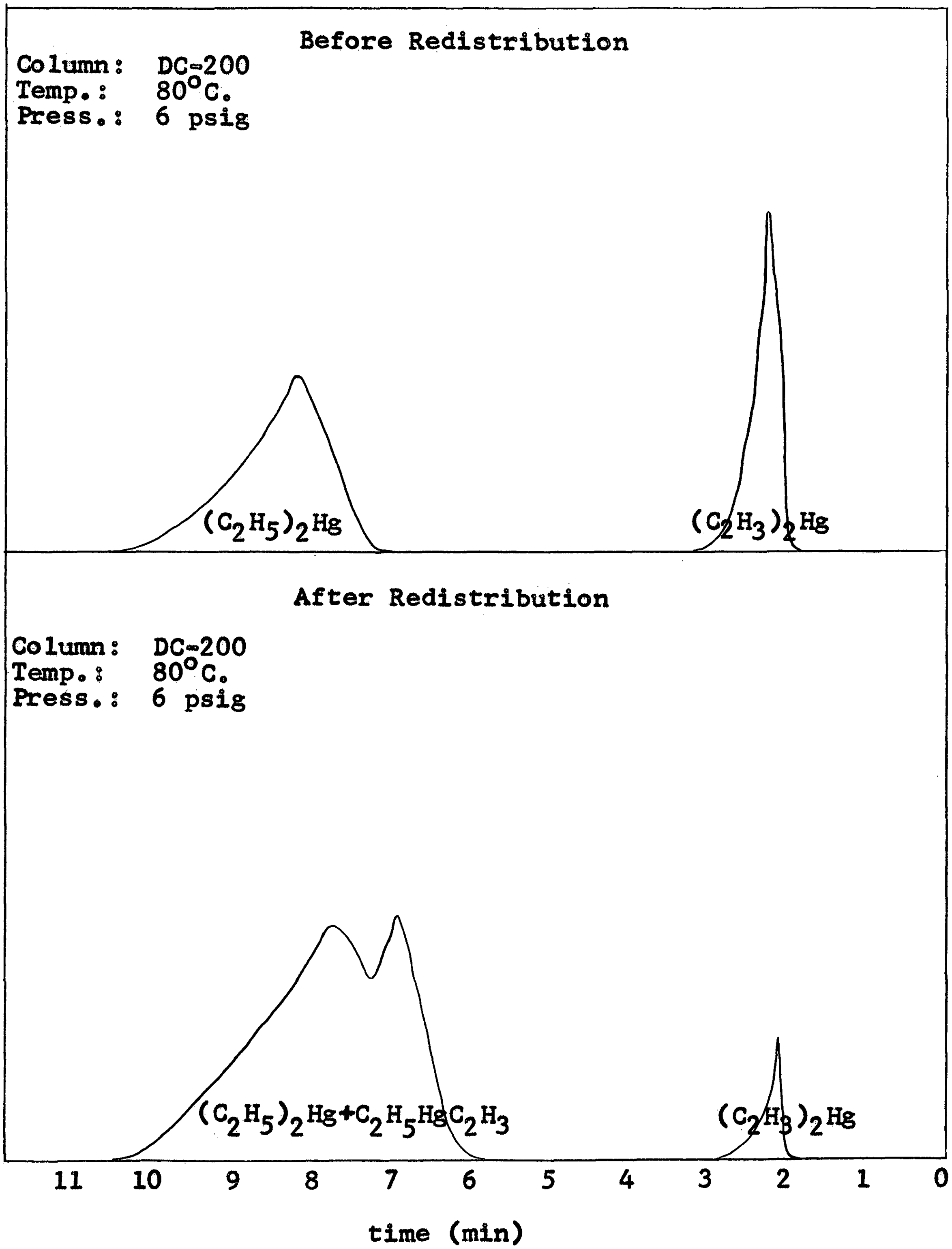


FIGURE 13. $(C_2H_3)_2Hg/(c\text{-}C_3H_5)_2Hg$

GAS-LIQUID CHROMATOGRAMS OF SYSTEM

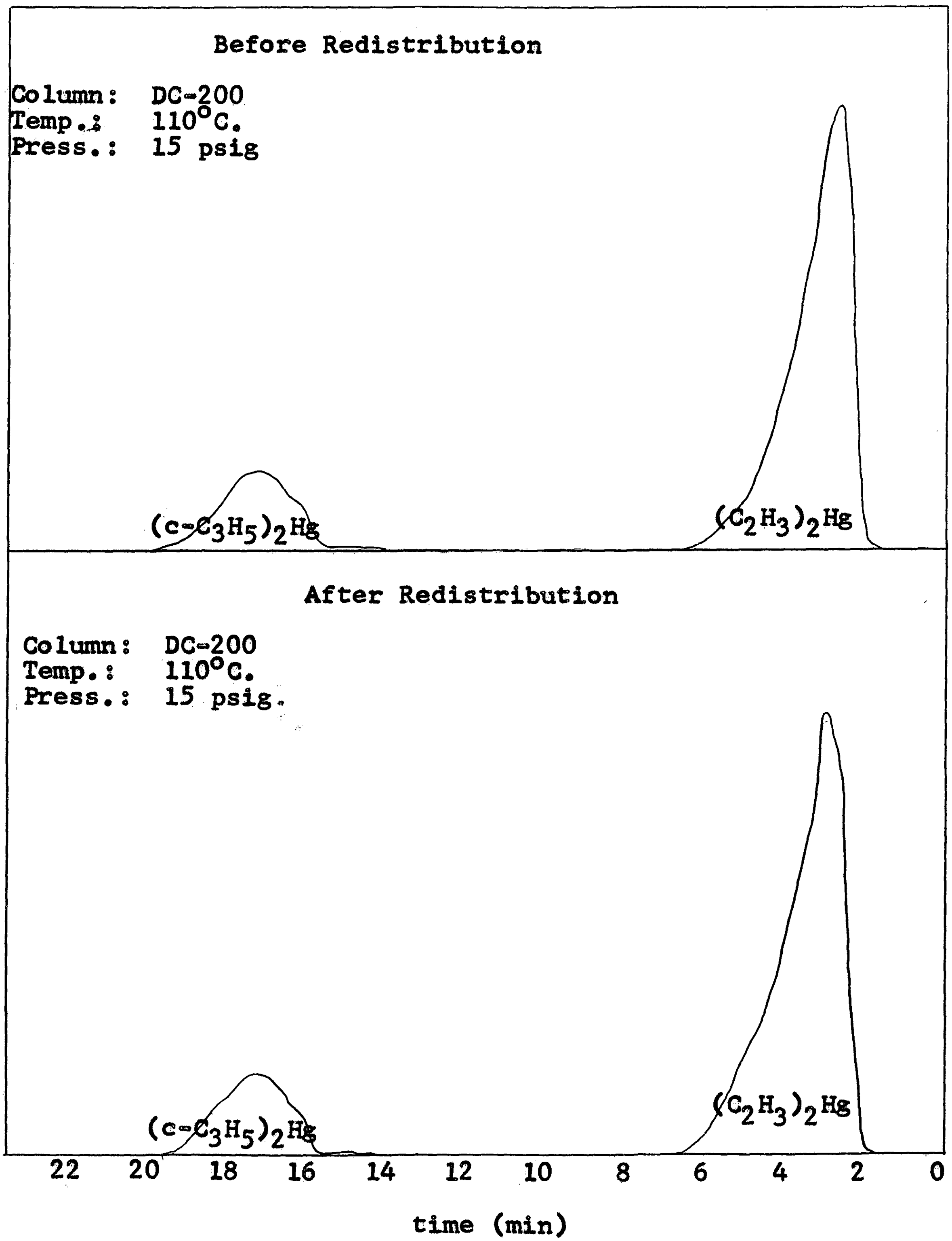


FIGURE 14.

GAS-LIQUID CHROMATOGRAMS OF $(C_2H_5)_2Hg/(n\text{-}C_3H_7)_2Hg$ SYSTEM

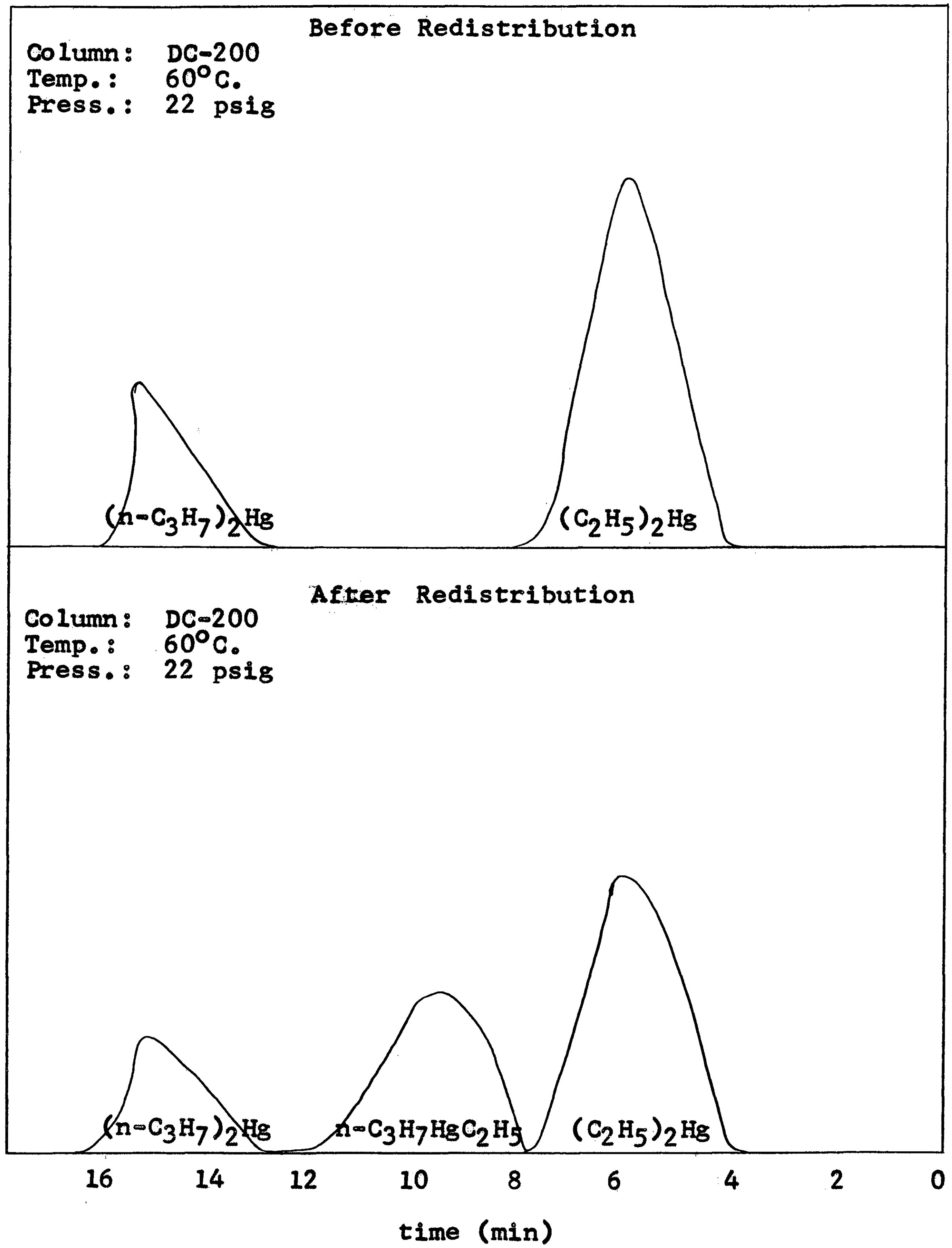


FIGURE 15

GAS-LIQUID CHROMATOGRAMS OF $(C_2H_5)_2Hg/(i\text{-}C_3H_7)_2Hg$ SYSTEM

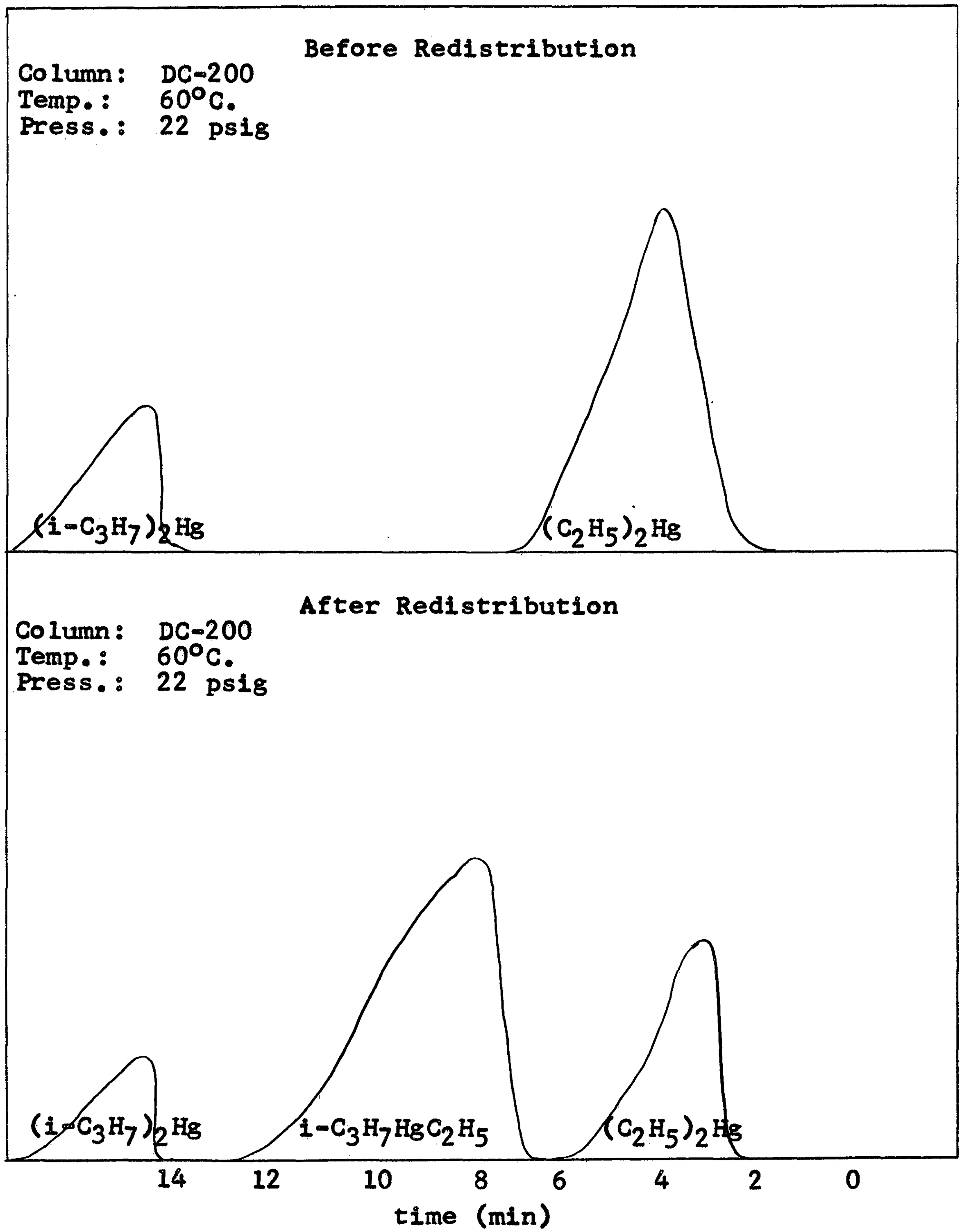


FIGURE 16

GAS-LIQUID CHROMATOGRAMS OF $(i\text{-}C_3F_7)_2Hg/(i\text{-}C_3H_7)_2Hg$ SYSTEM

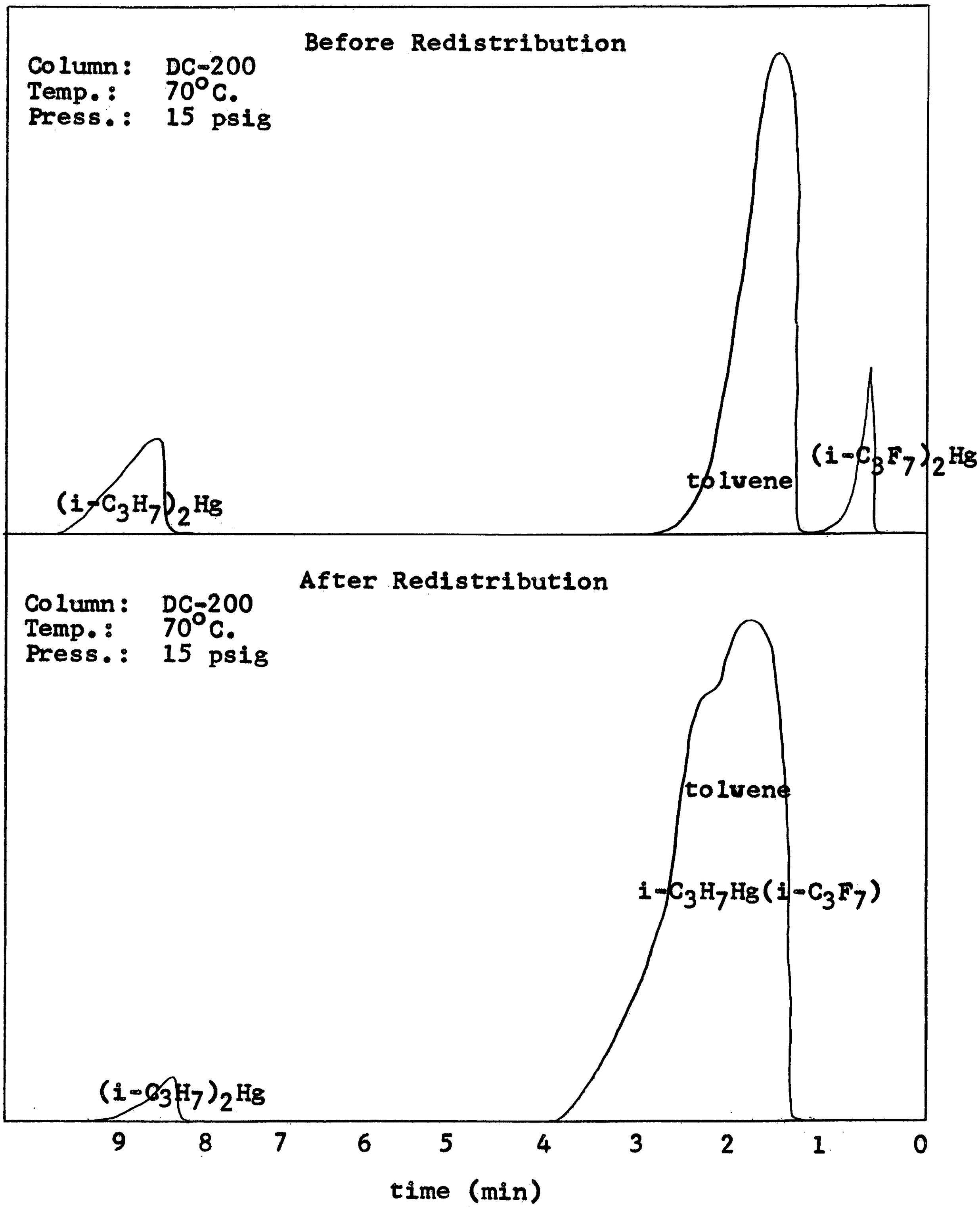


FIGURE 17

GAS-LIQUID CHROMATOGRAMS OF $(i\text{-}C_3F_7)_2Hg/(n\text{-}C_3H_7)_2Hg$ SYSTEM

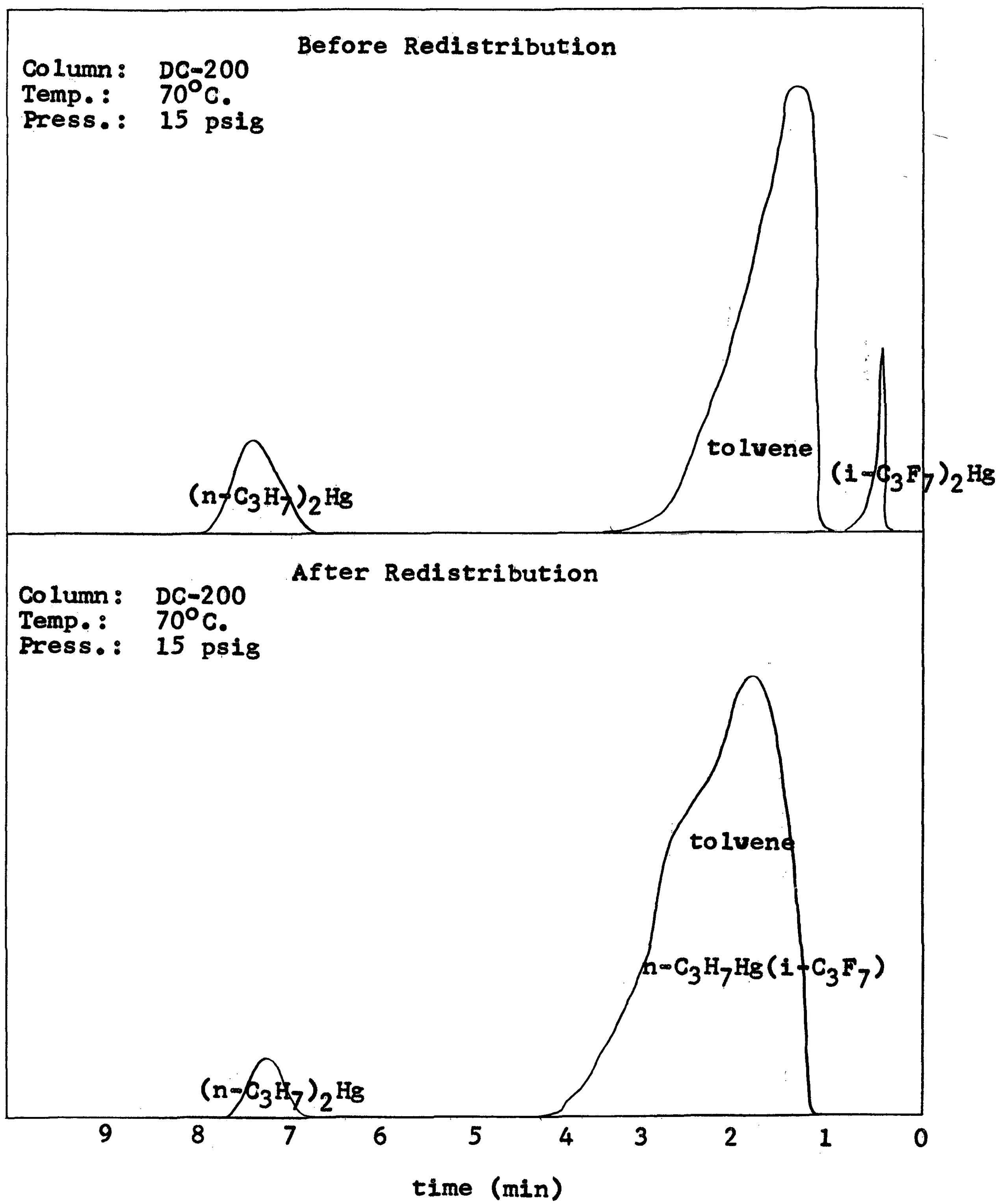


FIGURE 18

PHENYL PROTON NMR SPECTRA

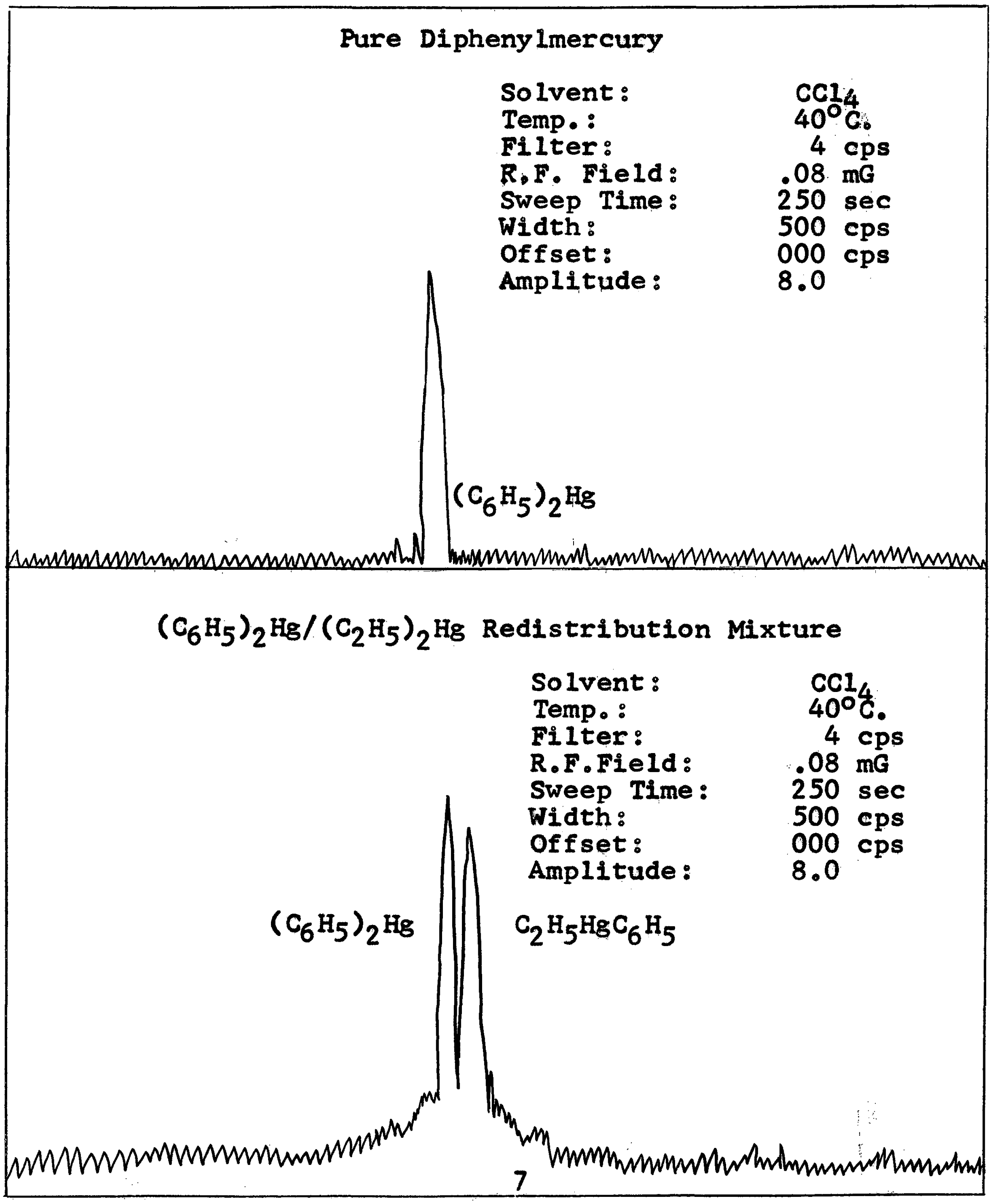


FIGURE 19

PHENYL PROTON NMR SPECTRA AND INTEGRALS

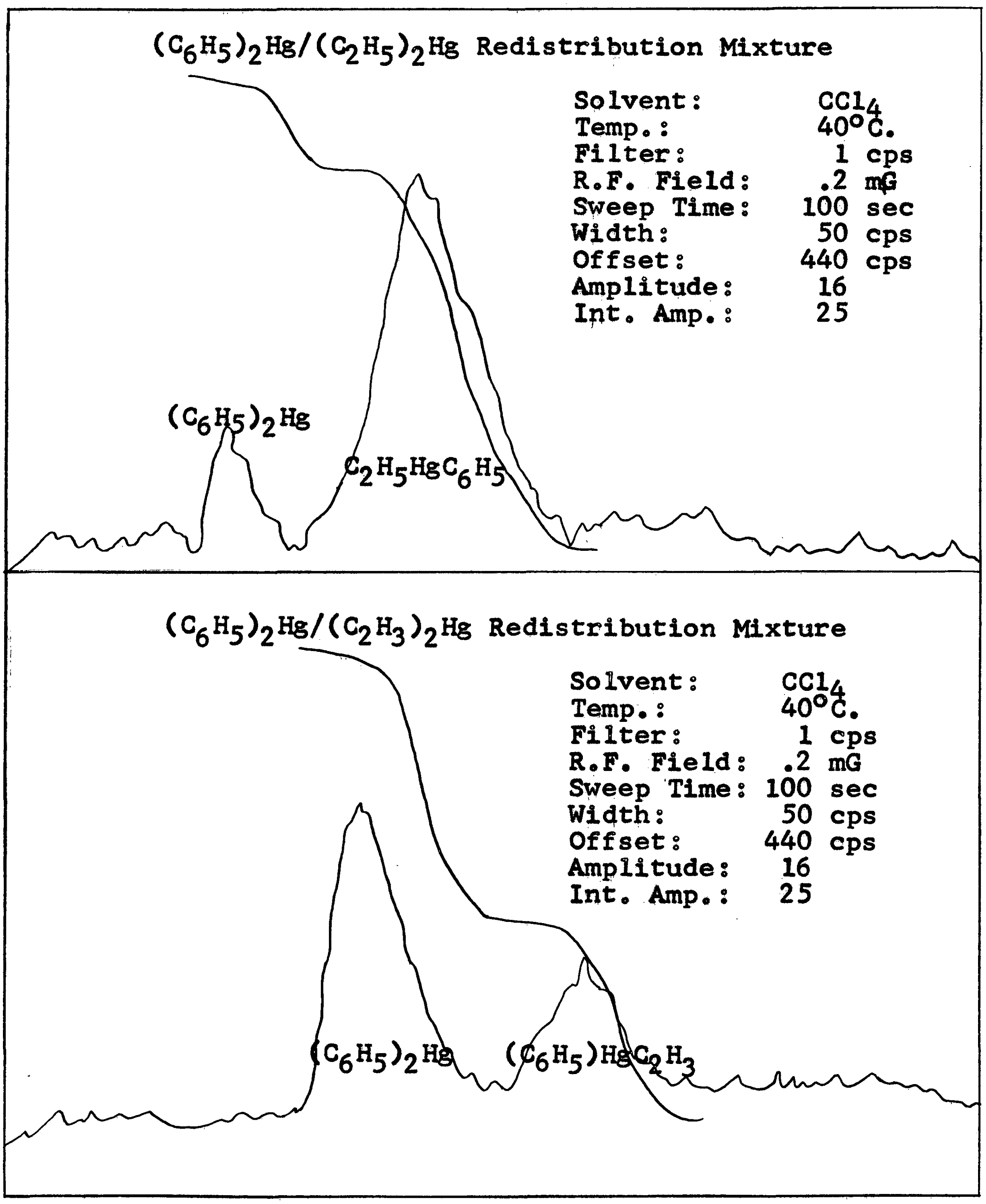


Table 4. $(CH_3)_2Hg/(C_2H_5)_2Hg$ Redistribution Results

Initial molar ratio CH_3/C_2H_5	Equilibrium % total mercury $(CH_3)_2Hg$	$CH_3HgC_2H_5$	$(C_2H_5)_2Hg$	K_{exp}
0.24	4.7	24.9	70.4	1.88
0.53	12.9	34.6	52.5	1.77
0.93	28.9	40.5	30.6	1.86
1.00	29.5	40.8	29.7	1.90
1.92	53.4	31.8	14.8	1.28
5.70	73.5	22.8	3.7	0.84
0.74*	24.5	39.1	36.5	1.71

$K_{exp} = 1.8$; $\Delta G_{dev} = + 0.6$ kcal/mole

* This sample was reacted in toluene solution.

Table 5. $(C_2H_5)_2Hg/(c\text{-}C_3H_5)_2Hg$ Redistribution Results

Initial molar ratio $C_2H_5/c\text{-}C_3H_5$	Equilibrium % total mercury $(C_2H_5)_2Hg$	$C_2H_5Hg(c\text{-}C_3H_5)$	$(c\text{-}C_3H_5)_2Hg$	K
0.24	2.0	62.5	35.5	55
0.75	6.0	83.5	10.5	111
1.00	7.4	86.0	6.6	151
1.00**	7.1	85.8	7.1	146
1.30	11.1	84.0	4.9	130
1.55	18.2	79.1	2.7	127
5.50	53.1	45.6	1.3	31

$K_{exp} = 100$; $\Delta G_{dev} = -2.3$ kcal/mole

** Initial sample was $c\text{-}C_3H_5HgC_2H_5$.

Table 6. $(C_2H_5)_2Hg/(C_2H_3)_2Hg$ Redistribution Results

Initial molar ratio C_2H_5/C_2H_3	Equilibrium % total mercury $(C_2H_5)_2Hg$	$C_2H_5HgC_2H_3$	$(C_2H_3)_2Hg$	K_{exp}
0.13	0.5	22.2	77.3	126
0.44	1.1	59.2	39.7	80
1.19	14.0	81.2	4.8	98
3.22	53.1	46.4	0.5	81
9.00	80.0	19.6	0.4	120

$K_{exp} = 100$; $\Delta G_{dev} = -2.3$ kcal/mole

Table 7. $(C_2H_3)_2Hg/(c\text{-}C_3H_5)_2Hg$ Redistribution Results

Under the conditions employed in this study, no evidence of redistribution could be found in this system after two weeks reaction time.

Table 8. $(C_2H_5)_2Hg/(C_6H_5)_2Hg$ Redistribution Results

Initial molar ratio C_2H_5/C_6H_5	Equilibrium % total mercury $(C_2H_5)_2Hg$	$C_2H_5HgC_6H_5$	$(C_6H_5)_2Hg$	K_{exp}
0.47	8.0	47.6	44.4	6.4
1.00*	23.4	53.2	23.4	5.2
1.26	29.7	52.2	18.1	5.0
1.71	38.7	48.8	12.5	4.9
3.88	62.6	33.8	3.6	5.1

$K_{exp} = 5.0$; $\Delta G_{dev} = -0.2$ kcal/mole

* Initial mixture was $C_2H_5HgC_6H_5$.

Table 9. $(C_2H_3)_2Hg/(C_6H_5)_2Hg$ Redistribution Results

Initial molar ratio C_2H_3/C_6H_5	Equilibrium % total mercury $(C_2H_3)_2Hg$	$C_2H_3HgC_6H_5$	$(C_6H_5)_2Hg$	K_{exp}
0.41	3.6	51.0	45.4	15.9
0.60	7.4	60.2	32.4	15.1
1.63	31.8	60.4	7.8	14.8
3.65	58.6	39.7	1.7	15.8

$K_{exp} = 15.5$; $\Delta G_{dev} = -1.0$ kcal/mole

Table 10. $(C_2H_5)_2Hg/(n-C_3H_7)_2Hg$ Redistribution Results

Initial molar ratio $C_2H_5/n-C_3H_7$	Equilibrium % total mercury $(C_2H_5)_2Hg$	$C_2H_5Hg(n-C_3H_7)$	$(n-C_3H_7)_2Hg$	K_{exp}
0.19	2.3	27.0	70.7	4.5
0.42	8.4	42.2	49.4	4.3
1.03	24.9	51.6	23.5	4.5
2.86	54.3	39.6	6.1	4.7
5.36	71.3	26.6	2.4	4.2

$K_{exp} = 4.4$; $\Delta G_{dev} = -0.1$ kcal/mole

Table 11. $(C_2H_5)_2Hg/(i-C_3H_7)_2Hg$ Redistribution Results

Initial molar ratio $C_2H_5/i-C_3H_7$	Equilibrium % total mercury $(C_2H_5)_2Hg$	$i-C_3H_7HgC_2H_5$	$(i-C_3H_7)_2Hg$	K_{exp}
0.41	7.2	43.6	49.2	5.3
1.50	34.3	51.4	14.3	5.4
3.24	57.6	37.6	4.8	5.1
7.85	78.4	20.6	1.0	5.4

$K_{exp} = 5.3$; $\Delta G_{dev} = -0.2$ kcal/mole

Table 12. $(n\text{-}C_3H_7)_2Hg/(i\text{-}C_3F_7)_2Hg$ Redistribution Results

Initial molar ratio $n\text{-}C_3H_7/i\text{-}C_3F_7$	Equilibrium % total mercury $(n\text{-}C_3H_7)_2Hg$	$n\text{-}C_3H_7Hg(i\text{-}C_3F_7)$	$(i\text{-}C_3F_7)_2Hg$
0.32	0.0	48.0	52.0
0.66	0.1	79.6	20.3
0.93	0.3	95.8	3.9
2.36	40.6	59.4	0.0
10.50	82.6	17.4	0.0

$K_{exp} > 10^3$; $\Delta G_{dev} > -4$ kcal/mole

Values for limiting reactant estimated from ratio of two major peaks and reaction stoichiometry.

Table 13. $(i\text{-}C_3H_7)_2Hg/(i\text{-}C_3F_7)_2Hg$ Redistribution Results

Initial molar ratio $i\text{-}C_3H_7/i\text{-}C_3F_7$	Equilibrium % total mercury $(i\text{-}C_3H_7)_2Hg$	$i\text{-}C_3H_7Hg(i\text{-}C_3F_7)$	$(i\text{-}C_3F_7)_2Hg$
0.60	0.1	74.8	25.1
0.96	0.7	96.4	2.9
1.10	4.9	94.8	0.3
1.75	27.2	72.8	0.0
2.61	44.8	55.2	0.0

$K_{exp} > 10^3$; $\Delta G_{dev} > -4$ kcal/mole

Values for limiting reactant estimated from ratio of two major peaks and reaction stoichiometry.

Table 14. Physical Properties of Bisorganomercury Compounds

Compound	Refractive Index (20/D)	B. P.	M. P.
$(CH_3)_2Hg$	1.54735	92-96°C.	---
$(C_2H_3)_2Hg$	---	156-7	---
$(C_2H_5)_2Hg$	1.54765		---
$(n\text{-}C_3H_7)_2Hg$	1.5170	189-91	---
$(i\text{-}C_3H_7)_2Hg$	1.5263		---
$(C_6H_5)_2Hg$	---	d. 306	125-6°C.

LITERATURE CITED

1. Salinger, R. M., and Mosher, H. M., Infra-red spectral studies of Grignard solutions: J. Am. Chem. Soc., v. 86, p. 1782-1786 (1964)

2. Dessy, R. E., and Handler, G. S., The constitution of the Grignard reagent: J. Am. Chem. Soc., v. 80, p. 5824-5826 (1958)

3. Dessy, R. E., Handler, G. S., Wotiz, J. H., and Hollingsworth, C. A., The constitution of the Grignard reagent: J. Am. Chem. Soc., v. 79, p. 3476-3477 (1957)

4. Muller, N., and Pritchard, D. E., Proton magnetic resonance spectrum of aluminum trimethyl dimer: J. Am. Chem. Soc., v. 82, p. 248-249 (1962)

5. Calingaert, G., Beatty, H. A., and Soroos, H., The redistribution reaction V. R_4Pb compounds: J. Am. Chem. Soc., v. 62, p. 1099-1104 (1940)

6. Calingaert, G., Soroos, H., and Hnizda, V., The redistribution reaction VII. Allyl compounds of mercury, tin, silicon, and zinc: J. Am. Chem. Soc., v. 62, p. 1107-1110 (1940)

7. Calingaert, G., and Beatty, H. A., The redistribution reaction I. The random intermolecular exchange of organic radicals: J. Am. Chem. Soc., v. 61, p. 2748-2754 (1939)

8. Van Wazer, J. R., Structural reorganization through ligand interchange: Amer. Sci., v. 50, p. 450-472 (1962)

9. Van Wazer, J. R., and Moedritzer, K., Scrambling of methoxy, dimethylamino, and chloro groups on silicon: Inorg. Chem., v. 3, p. 268-273 (1964)

10. Van Wazer, J. R., and Moedritzer, K., Exchange of parts between molecules at equilibrium I. , -disubstituted polymethylsiloxanes: J. Am. Chem. Soc., v. 86, p. 802-807 (1964)

11. Leffler, J. E., and Grunwald, E., Rates and equilibria of organic reactions: New York, John Wiley and Sons, Inc., p. 139-142 (1963)

12. Calingaert, G., and Beatty, H. A., The redistribution reaction: Organic Chemistry, v. 2, Gilman, H., ed., New York, John Wiley and Sons, Inc., p. 1806-1820 (1943)

13. Stock, A., and Somieski, C., Siliciumwasserstoffe VI. Chlorierung und Methylierung des Monosilans: Ber., v. 52, p. 695-724 (1919)

14. Whitmore, F. C., Organic compounds of mercury: New York, The Chemical Catalogue Company, Inc., p. 65-67 (1921)

15. Dessy, R. E., The constitution of organoberyllium halides: J. Am. Chem. Soc., v. 82, p. 1580-1582 (1960)

16. Gilman, H., and Miles, D. H., Disproportionation reaction of diphenylsilane in the absence of any added catalyst: J. Org. Chem., v. 23, p. 326-328 (1958)

17. Zemany, P. D., and Price, F. P., Kinetics and thermodynamic properties of the disproportionation of methylchlorosilanes: J. Am. Chem. Soc., v. 70, p. 4222-4226 (1948)

18. Russell, G. A., Catalysis by metal halides II. The disproportionation of trimethylsilane, phenyltrimethylsilane, and bromotrimethylsilane: J. Am. Chem. Soc., v. 81, p. 4825-4831 (1959)

19. Bailey, D. L., and Pines, A. N., Reactions of allylic silicon compounds: Ind. Eng. Chem., v. 46, p. 2363-2367 (1954)

20. Rausch, M. D., and Van Wazer, J. R., Exchange reactions and NMR analysis of some organomercury compounds: Inorg. Chem., v. 3, p. 761-766 (1963)

21. Dessy, R. E., Kaplan, F., Coe, G. R., and Salinger, R. M., Exchange reactions in Group II organometallic systems: J. Am. Chem. Soc., v. 85, p. 1191-1199 (1963)

22. Chamber, R. D., Coates, G. E., Livingstone, J. G., and Musgrave, W. R., The preparation and study of some pentafluorophenylmercury compounds: J. Chem. Soc. (London), p. 4367-4371 (1962)

23. Lockhart, J. C., Redistribution and exchange reactions in Groups IIB-VIIB: Chem. Rev., v. 65, p. 131-151 (1965)

24. Quane, D., and Bottei, R. S., Organogermanium chemistry: Chem. Rev., v. 63, p. 403-442 (1963)

25. Zeiss, H., Organometallic chemistry: New York, Reinhold Publishing Company, (1960)

26. Coates, G. E., Organometallic compounds: London, Metheun and Company, (1956)

27. Russell, G. A., Catalysis by metal halides I. Mechanism of the disproportionation of ethyltrimethylsilane: J. Am. Chem. Soc., v. 81, p. 4815-4825 (1959)

28. Charman, H. B., Hughes, E. D., Ingold, C. K., and Thorpe, F. G., Mechanism of electrophillic substitution at a saturated carbon atom. III. Kinetics, stereochemistry, and mechanism of the three-alkyl mercury-exchange reaction: J. Chem. Soc. (London), p. 1121-1133 (1961)

29. Dessy, R. E., Unpublished presentation: Meeting on Organometallics, New York Academy of Science, New York, (1964)

30. Kharasch, M. S., and Marker, R., The decomposition of unsymmetrical organomercuric compounds: A method of establishing the relative degree of electromegativity of organic radicals I.: J. Am. Chem. Soc., v. 48, p. 3130-3143 (1926)

31. Kharasch, M. S., and Flenner, A. L., The decomposition of unsymmetrical organomercuric compounds: A method of establishing the relative degree of electronegativity of organic radicals II.: J. Am. Chem. Soc., v. 54, p. 674-692 (1932)

32. Kharasch, M. S., Pines, H., and Levine, J. H., the decomposition of unsymmetrical organomercuric compounds: A method of establishing the relative degree of electronegativity of organic radicals III.: J. Org. Chem., v. 3, p. 347-354 (1939)

33. Kharasch, M. S., and Swartz, S., The decomposition of unsymmetrical organomercuric compounds: A method of establishing the relative degree of electronegativity of organic radicals IV.: J. Org. Chem., v. 3, p. 405-408 (1939)

34. Kharasch, M. S., Legault, R. P., and Sprowls, W. R., The decomposition of unsymmetrical organomercuric compounds: A method of establishing the relative degree of electronegativity of organic radicals V.: J. Org. Chem., v. 3, p. 409-413 (1939)

35. Meek, J. S., and Osuga, D. T., Bromocyclopropane: Org. Syn., v. 43, p. 9-12 (1963)

36. Reynolds, G. F., Dessy, R. E., and Jaffe, H. H., Dicyclopropylmercury and divinylmercury: J. Org. Chem., v. 23, p. 1217-1218 (1958)

37. Aldrich, P. E., Howard, E. G., Linn, W. J., Middleton, W. J., and Sharkey, W. H., Secondary and tertiary perfluororganomercury compounds: J. Org. Chem., v. 28, p. 184-188 (1963)

38. Kaufman, H. C., Handbook of organometallic compounds: Princeton, New Jersey, D. Van Nostrand Company, Inc., (1961)

39. Hilpert, S., and Gruttner, G., Uber gemischte Quecksilber-dialkyle: Ber., v. 48, p. 906-915 (1915)