

this ion is A. Doering, *et al.*,<sup>11</sup> have shown this ion to be the terminal product of a Friedel-Crafts methylation of methylbenzenes. The conjugate base, C<sub>13</sub>H<sub>20</sub>, B, is stronger than hexamethylbenzene and probably would not be desorbed from the catalyst. This heptamethylbenzenonium ion can react *via* changes in ring size and undergo the paring reaction as previously suggested.

The yield of methane and ethane in the paring reaction is low because of the difficulty of cleaving a methyl or ethyl group from the ring. Propyl groups crack somewhat more readily to form propane. However, a side chain containing four or more carbons cleaves rapidly. Although steady state concentrations of cationic intermediates with a butyl side chain may be very low, once these species are formed cracking occurs readily.

In the presence of nickel sulfide on silica-alumina and hydrogen, some hydrogenation of aromatics to naphthenes occurs. It is therefore possible that with this catalyst part of the C<sub>9</sub>-naphthenes and isoparaffins in the product may be formed by means of a naphthenic intermediate, hexamethylcyclohexyl cation. This ion would isomerize to give products with different side chains. The studies of Pines and Shaw<sup>12</sup> show that a similar isomerization of ethylcyclohexane proceeds through a carbonium ion mechanism involving repeated ring expansions and contractions with eventual attainment of equilibrium isomer distribution. Thus, if a hexamethylcyclohexyl cation intermediate is formed, one might expect rapid establishment of equilibrium among its isomers, followed by cracking of the C<sub>4</sub>-side chains. The reactions of

(11) W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards and G. Laber, *Tetrahedron*, **4**, 178 (1958).

(12) H. Pines and A. W. Shaw, *J. Am. Chem. Soc.*, **79**, 1474 (1957).

hexamethylcyclohexane have been studied also, and the results, which confirm this hypothesis, will be presented in a later publication.

Because the quantity of naphthene formed is relatively small, particularly in experiment C, a mechanism involving only naphthenes as intermediates is inadequate. We propose, therefore, that a major fraction of the product is formed directly from the aromatic through a route involving changes in ring size. Additional support for this conclusion is that hexamethylbenzene undergoes the paring reaction with the silica-alumina support alone and forms no naphthenes.

The mechanism postulated for the paring reaction indicates that it can occur only with aromatics containing at least 10 carbon atoms because 10 carbon atoms is the minimum necessary to form isobutane and still leave an aromatic nucleus. This is consistent with the experimental data obtained with the C<sub>6</sub>- to C<sub>9</sub>-aromatics where the paring reaction is found to be minor. Some paring can occur with lower molecular weight aromatic feeds, such as mesitylene, because the methyl transfer reaction forms some molecules sufficiently large to undergo paring.

Small amounts of alkylbenzenes other than methylbenzenes with carbon numbers of 11 and 12 can be detected in the product, proving that side chain growth does occur. However, the products from the paring reaction of hexamethylbenzene are characterized by the absence of large amounts of aromatics having ethyl and propyl side chains. This fact suggests that the adsorbed species that are undergoing side chain growth by successive ring contractions and expansions usually do not desorb from the catalyst before they have grown a sufficiently large side chain which can be eliminated by cracking.

The hydrocracking of other aromatic and naphthenic hydrocarbons under these conditions will be described in future publications.

**Acknowledgment.**—This study is an outgrowth of the pioneering work of John W. Scott, Jr., on the use of this catalyst in petroleum hydrocracking.

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## Carbonyl Reactions. XI. Deuterium Exchange in the Acid-catalyzed Isomerization of *cis*-Benzalacetophenone<sup>1</sup>

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In 60% aqueous dioxane, *cis*-benzalacetophenone is rapidly isomerized to *trans*-benzalacetophenone by 3-molar sulfuric acid. Using sulfuric acid-*d*<sub>2</sub> in dioxane-deuterium oxide, no deuterium is introduced during the isomerization. The isomerization is faster in sulfuric acid-*d*<sub>2</sub> than in ordinary sulfuric acid. These results confirm the previously proposed mechanism, which involves as the rate-determining step the addition of water to the oxonium salt of *cis*-benzalacetophenone. The mechanism of hydration of  $\alpha,\beta$ -unsaturated aldehydes and ketones is discussed in light of these results.

### Introduction

In the previous paper of this series,<sup>1</sup> the isomerization of *cis*-benzalacetophenone to *trans*-benzal-

acetophenone by acid was investigated under a variety of conditions. The rate of isomerization did not parallel the acidity function *H*<sub>0</sub>. It was also shown that  $\beta$ -phenyl- $\beta$ -hydroxypropio-phenone must be excluded as an intermediate in the isomerization, since the rate of dehydration is

(1) Previous report, D. S. Noyce, W. A. Pryor and P. A. King, *J. Am. Chem. Soc.*, **81**, 5423 (1959).

(2) National Institutes of Health Post-Doctoral Fellow, 1959-1960.

slower than the rate of isomerization. Further, the dehydration process is accompanied by competing cleavage to benzaldehyde and acetophenone. The proportion of cleavage increases at higher acidities.

It was proposed that the most satisfactory interpretation of these results is a mechanism in which the rate-controlling process is the addition of water to the conjugate acid (oxonium salt) of *cis*-benzalacetophenone. Following this slow step, rapid rotation about the single bond and loss of water occur.

Further confirmation for this mechanism has been sought in a study of the fate of *cis*-benzalacetophenone in sulfuric acid- $d_2$  solution.

### Results

Acetophenone- $d_3$  (I) was prepared by exchange of the labile hydrogens with deuterium oxide. After four exchanges 95% of the available hydrogen had been replaced. Compound I was converted to *trans*-benzalacetophenone- $\alpha$ - $d$  (II) by condensation with benzaldehyde in deuterium oxide and sodium deuterioxide. In this process further enrichment takes place, since the rate of abstraction of a hydrogen from acetophenone is much more rapid than the rate of the condensation step. The II formed had 0.975 deuterium atom per mole. The infrared spectrum of II (Fig. 1, curve B) shows very marked differences in the 1100–900  $\text{cm}^{-1}$  region when compared with normal *trans*-benzalacetophenone (Fig. 1, curve A). There is a notable absence of the characteristic bands of ordinary benzalacetophenone in the 1100–900  $\text{cm}^{-1}$  region. The C–D stretching vibration is extremely weak in both acetophenone- $d_3$  and II.<sup>3</sup>

The conditions chosen for the isomerization were somewhat different from those used in the previous kinetic study, dictated by the necessity of having present in a reasonably small volume of solution sufficient material for facile isolation. Aqueous dioxane was chosen as the co-solvent with sulfuric acid as the catalyst, since indicator acidity function values have been measured in this solvent.<sup>4</sup> It has the further advantage of minimizing the required preparations of isotopic species.

By extrapolating from the previous kinetic data, conditions were chosen which would be expected to lead to 90% isomerization of *cis*-benzalacetophenone.

It was first shown that *trans*-chalcone- $\alpha$ - $d$  (II) is stable under these chosen conditions in dioxane- $\text{H}_2\text{O}$ - $\text{H}_2\text{SO}_4$  (cf. Fig. 1, spectrum C). This serves to show not only that the isolation procedure will cause no aberration in the results, but also that there is no rapid exchange of the  $\alpha$ -hydrogen in  $\alpha,\beta$ -unsaturated ketones.

Secondly, *cis*-benzalacetophenone was treated with sulfuric acid- $d_2$  under these conditions. A satisfactory yield of *trans*-benzalacetophenone was isolated, demonstrating that the choice of conditions was suitable. The spectrum (Fig. 1, curve D) of the *trans*-benzalacetophenone isolated showed

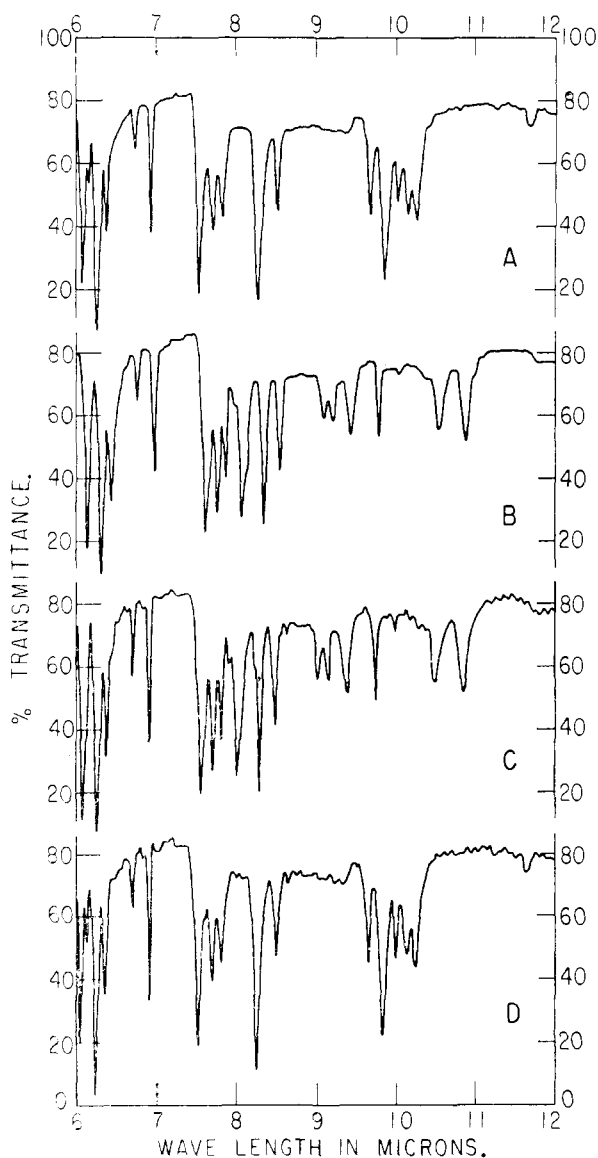


Fig. 1.—Infrared spectra of benzalacetophenones. All spectra were determined in  $\text{CCl}_4$  solution at a concentration of 40 mg./ml.; using 0.1-mm. NaCl cells: A, authentic *trans*-benzalacetophenone; B, *trans*-benzalacetophenone- $\alpha$ - $d$  (II); C, *trans*-benzalacetophenone- $\alpha$ - $d$  after treatment with  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$ -dioxane; D, *trans*-benzalacetophenone from the isomerization of *cis*-benzalacetophenone in  $\text{D}_2\text{SO}_4$ - $\text{D}_2\text{O}$ -dioxane.

no evidence whatsoever for the incorporation of deuterium.

These results make it abundantly clear that the isomerization proceeds *via* a pathway in which the  $\alpha$ -hydrogen retains its complete integrity, and in no way becomes part of an equivalent pair.

**Rate of Isomerization in Sulfuric Acid- $d_2$ .**—To provide additional information, a comparison of the rates of the isomerization of *cis*-benzalacetophenone in both sulfuric acid and sulfuric acid- $d_2$  has been made. The mixed solvent 95% water-5% dioxane has been found to be extremely useful<sup>5</sup>

(5) Full details of studies carried out in this solvent will be reported shortly; unpublished studies of Dr. M. J. Jorgenson.

(3) Cf. S. A. Francis, *J. Chem. Phys.*, **9**, 942 (1951).

(4) C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt and C. A. Vernon, *J. Chem. Soc.*, 2327 (1957).

for studies of acid-catalyzed reactions. The results obtained are reported in Table I.

TABLE I  
RATE OF ISOMERIZATION OF *cis*-CHALCONE IN 5% AQUEOUS DIOXANE BY SULFURIC ACID AT 25.00°

Acid, <i>M</i>	$k \times 10^6$ , sec. <sup>-1</sup>	$k_D/k_H$
H <sub>2</sub> SO <sub>4</sub> , 3.06	3.15	
D <sub>2</sub> SO <sub>4</sub> , 3.06	6.13	1.94
D <sub>2</sub> SO <sub>4</sub> , 3.06	5.98	1.90

The faster isomerization in D<sub>2</sub>SO<sub>4</sub>-D<sub>2</sub>O clearly rules out a mechanism in which the rate-determining process is the attack of a proton on the  $\alpha$ -carbon. The significance of this exclusion is most clearly realized, if one considers the single fact of lack of smooth correlation with the acidity function.<sup>1</sup> Such a failure *could* be taken as evidence for a rate-determining proton transfer. The kinetic isotope effect also eliminates the possibility (most unlikely at best) that a highly stereospecific sequence (initiated by proton attack at the  $\alpha$ -carbon) was responsible for the isotopic composition of the *trans*-chalcone discussed above.

Another relation supports these conclusions further. The acid-catalyzed isomerization of *cis*-cinnamic acid is several orders of magnitude slower<sup>6</sup> than the isomerization of *cis*-chalcone. Were both reactions to involve a proton attack at the double bond, it would be expected that they should occur with similar facility, since the electron density about the double bond is similar. These results, then, clearly support the mechanism proposed earlier, in which the rate-determining process is the addition of water to the conjugate acid of *cis*-benzalacetophenone.

### Discussion

It is instructive to compare the mechanism of this *cis-trans* isomerization with the hydration-dehydration equilibria studied some time ago by Lucas and co-workers.<sup>7-11</sup> Pressman and Lucas<sup>10</sup> observed that the rate of reaction for acrolein is several orders of magnitude larger than for allyl alcohol or acrylic acid. Similar observations were made for crotonaldehyde and crotonic acid<sup>7,8</sup> and for dimethylacrylic acid and dimethylacrolein.<sup>9,11</sup> This of course implies that the enol or a closely related species is intimately concerned with the mechanistic process by which the equilibrium is established.

Application of the mechanism of *cis-trans* isomerization here developed leads to the following very important conclusion when applied to the hydration step.

The sequence of steps, protonation and addition of water, must be fast relative to the formation of the hydroxyketone. This follows from the fact that the hydroxyketone is not an intermediate in the *cis-trans* isomerization. Furthermore, the rate of rotation and loss of the elements of water are more rapid than ketonization. Thus by a

process of exclusion the rate-determining process for the hydration of acrolein is the ketonization of the hydroxyenol.

By the principle of microscopic reversibility, the mechanism of dehydration involves enolization as the rate-determining step. This is in complete accord with the conclusions drawn by Noyce and Reed<sup>12</sup> for the general mechanism for dehydration of hydroxyketones.

Finally this picture of the mechanism has been developed without ultimate dependence upon the form of the acidity dependence. In other words, the Hammett-Zucker hypothesis has not been invoked to provide the entire supporting framework.

It is therefore interesting to point out that all of the reactions discussed here appear to involve rate-acidity correlations which do not follow  $H_0$  but instead are more closely related in behavior to the enolization of acetophenone.

Thus a general picture involving enolic species has been developed for the dehydration of  $\beta$ -hydroxyketones, the hydration of  $\alpha,\beta$ -unsaturated aldehydes and ketones and for *cis-trans* isomerization of  $\alpha,\beta$ -unsaturated ketones. Only in those instances where an overwhelming stabilization of a carbonium ion is possible (*e.g.*, the dehydration of 4-(*p*-methoxyphenyl)-4-hydroxy-2-butanone)<sup>12</sup> does here appear to be a change from this general pattern.

### Experimental<sup>13</sup>

$\alpha,\alpha,\alpha$ -*d*<sub>3</sub>-Acetophenone (I).—Modification of the procedure of Emmons and Hawthorne<sup>14</sup> by the elimination of the cosolvent resulted in a simplified procedure.<sup>15</sup> A heterogeneous mixture of 10 ml. of acetophenone and 10 ml. of deuterium oxide, to which about 0.1 g. of anhydrous potassium carbonate had been added, was refluxed overnight. The deuterated acetophenone was transferred by pipet to a fresh portion of deuterium oxide. Four exchanges were carried out, and the process was operated in a countercurrent fashion. After the final exchange, the crude acetophenone-*d*<sub>3</sub> was taken up in anhydrous ether, dried and distilled, b.p. 87.0–87.3° (11 mm.). The infrared spectrum (5% in CHCl<sub>3</sub>) showed no strong C–D stretching vibration, but the appearance of prominent new bands at 1105, 1000 and 985 cm.<sup>-1</sup>. Bands at 1420, 1355 and 953 cm.<sup>-1</sup> in the spectrum of ordinary acetophenone disappeared, and there were several additional bands which showed changed intensities. Analysis of I by mass spectra<sup>13</sup> showed 0.2% *d*<sub>4</sub>, 89.16% *d*<sub>3</sub>, 8.2% *d*<sub>2</sub>, 0.6% *d*<sub>1</sub> and 1.4% *d*<sub>0</sub>.

*trans*-1-Benzoyl-1-*a*-2-phenylethene (Chalcone- $\alpha$ -*d*) (II).—Sodium, 1.25 g., was added in small pieces to 20 ml. of deuterium oxide. To the cooled solution of sodium deuterioxide 5.2 g. of acetophenone-*d*<sub>3</sub> in 15 ml. of anhydrous dioxane was added, and immediately thereafter 4.6 g. of freshly distilled benzaldehyde was introduced in one portion. The solution was stirred at room temperature for 18 hours. The layers were separated, and the aqueous layer extracted with ether. The combined ether and dioxane extracts were dried, and distilled to afford a main fraction, b.p. 179–180° (2.8 mm.), 4.36 g. (48%), m.p. 53.5–55.2°. A small sample was crystallized from aqueous ethanol; m.p. 55.6–56.6°. The infrared spectrum (Fig. 1, curve B) showed bands at 1242, 1100, 1085, 1060, 1022, 955 and 920 cm.<sup>-1</sup> absent in authentic benzalacetophenone, and the absence of bands at 1640, 1030, 1015, 996, 984, 972 present

(12) D. S. Noyce and W. L. Reed, *ibid.*, **80**, 5539 (1958).

(13) Melting points are corrected. Infrared spectra were determined with a Baird model B infrared spectrophotometer. We wish to express our appreciation to the Shell Development Co. for their aid in determining the mass spectra.

(14) W. D. Emmons and M. F. Hawthorne, *J. Am. Chem. Soc.*, **78**, 5593 (1956).

(15) Suggested by A. Streitwieser, Jr.

(6) Unpublished results of P. A. King, W. L. Reed and H. Avarbock.

(7) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **59**, 1461 (1937).

(8) D. Pressman and H. J. Lucas, *ibid.*, **61**, 2271 (1939).

(9) D. Pressman and H. J. Lucas, *ibid.*, **62**, 2069 (1940).

(10) D. Pressman and H. J. Lucas, *ibid.*, **64**, 1953 (1942).

(11) H. J. Lucas, W. T. Stewart and D. Pressman, *ibid.*, **66**, 1818 (1944).

in authentic benzalacetophenone. The mass spectrum showed 0.3%  $d_2$ , 97.2%  $d_1$  and 1.4%  $d_0$  material.

*cis*-Benzalacetophenone was prepared by the reduction of phenylbenzoylacetylene, using Lindlar catalyst; m.p. 45.8–46.9°.

Sulfuric acid- $d_2$  was prepared by cautiously distilling sulfur trioxide into deuterium oxide.

**Chalcone- $\alpha$ - $d_1$  in Sulfuric Acid-Dioxane Solution.**—To a solution of 8 ml. of 9.0 *M* sulfuric acid in 12 ml. of dioxane was added 0.3 g. of chalcone- $\alpha$ - $d_1$ . The solution was maintained at 50° for 75 minutes, cooled to room temperature and extracted with three 30-ml. portions of ether. The ether was removed under reduced pressure, and the residue crystallized from aqueous ethanol. The product obtained weighed 0.13 g. (43%), m.p. 55.4–56.2°. The infrared spectrum (curve C) of this material showed no change from the spectrum of the original chalcone- $\alpha$ - $d_1$ , indicating no exchange of the  $\alpha$ -deuterium during the reaction period or the isolation procedure. The mass spectrum showed 0.3%  $d_2$ , 98.5%  $d_1$  and 0.9%  $d_0$ .

**The Isomerization of *cis*-Chalcone in Sulfuric Acid- $d_2$ -Dioxane.**—To a solution of 12.42 g. of 9.08 *M* sulfuric acid- $d_2$  ( $d^{22}$ , 1.5795) in 12 ml. of dioxane (distilled from calcium hydride) was added 0.3 g. of *cis*-chalcone. The resulting homogeneous solution was maintained at 50° for 72 minutes, cooled to room temperature and extracted

with three 30-ml. portions of ether. The combined extracts afforded an oily product after removing the solvent *in vacuo*. The crude chalcone was crystallized from aqueous ethanol; m.p. 56.6–57.3°, yield 0.129 g. (43%). The infrared spectrum of this material (curve D, Fig. 1) was completely superimposable upon the spectrum of authentic *trans*-chalcone, indicating that no deuterium had been introduced during the isomerization process.

**Kinetic Measurements.**—The rate of isomerization of *cis*-benzalacetophenone was measured as described previously,<sup>1</sup> by following the changes in ultraviolet absorption with a Beckman DU spectrophotometer equipped with a thermostated cell compartment. Solutions were prepared by taking sulfuric acid of the desired concentration and adding the requisite amount of a solution of *cis*-chalcone in dioxane.

**Acknowledgments.**—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We wish also to express our appreciation for the assistance of the Shell Development Co. in determining the mass spectral data reported.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

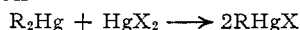
## The Mechanism of the Reaction of Mercuric Iodide with Bis-organomercury Compounds

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The rates of reaction of diphenylmercury with mercuric iodide in a variety of solvents, and a comparison of the ultraviolet spectra of the starting materials and the thermodynamics of reaction lead to some interesting conclusions concerning transition state shape. Phenylethylmercury has been found to react with  $\text{Hg}^{203}\text{Cl}_2$  to yield statistical distribution of tag in the products,  $\text{C}_6\text{H}_5\text{HgCl}$ ,  $\text{EtHgCl}$ —distribution which, it is shown, must have occurred in the transition state. By comparison with reactions of mercuracycloheptane and bis-*o*-phenylenedimercury, a transition state consistent with all of the known facts is presented.

During the past few years considerable effort has been expended<sup>2–5</sup> on the elucidation of the mechanism of the electrophilic substitution that occurs in the reaction



The work of Winstein,<sup>2</sup> Jensen<sup>4</sup> and Charman<sup>5</sup> indicates that the substitution occurs with retention of configuration at the attacked carbon, and there seems to be little doubt that the reaction indeed involves front-side attack.<sup>3</sup>

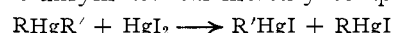
Charman<sup>5</sup> has described possible mechanisms for the reaction which he terms SE1, SE2 and SEi.

Dessy and Lee<sup>6</sup> suggested that the reaction involves a four-center transition state arising from molecular or ion pair attack.

In all of the investigations to date the effect of the solvent upon the shape of the reacting species has been neglected. Wright<sup>7</sup> has shown by dipole moment measurements that the bis-organomercury compounds are not linear in most solvent systems,

and indeed exhibit a C–Hg–C bond angle of approximately 120°, even in non-coordinating solvents such as benzene.

In addition, a kinetic investigation of the reaction of an unsymmetrical mercury compound has



not been attempted—an investigation which should shed some light on the controversy concerning the electronegativity sequence established by Kharasch.<sup>8</sup>

### Experimental

**Kinetics.**—The kinetic measurements were made as previously described.<sup>6</sup>

**Solvents.**—Spectral grade dioxane and cyclohexane, and analytical reagent ethanol and benzene were used throughout the investigation. They were purified by passage through 4X Molecular Sieve, Linde Co.

**Organomercury Compounds.**—Diphenylmercury: Distillation Products Industries No. 3868, recrystallized from ethanol; diethylmercury, prepared as previously described.<sup>9</sup>

Phenylethylmercury: Ethylmercuric chloride (26.5 g., 0.1 mole) was slowly added to 0.1 mole of phenyllithium (prepared from phenyl bromide and lithium) in 200 ml. of ether-benzene at 0°. The reaction was allowed to proceed at 0° overnight, and then hydrolyzed with water-ice. The organic layer was taken up in excess ether, dried over sodium sulfate, and filtered. Removal of solvent and distillation under reduced pressure yielded 13.0 g. (0.042 mole, 42%) of phenylethylmercury, b. p. 107–108° (5 mm.). Infrared

(8) M. S. Kharasch and A. L. Flenner, *J. Am. Chem. Soc.*, **54**, 576 (1932).

(9) R. E. Dessy and G. F. Reynolds, *ibid.*, **81**, 2683 (1959).

(1) National Science Foundation Predoctoral Research Fellows.

(2) S. Winstein, T. G. Traylor and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 3741 (1955).

(3) S. Winstein and T. G. Traylor, **78**, 2597 (1956).

(4) F. R. Jensen, L. H. Gaithe, L. D. Whipple and D. K. Wedergaertner, Abstracts, 135th Meeting of the American Chemical Society, Boston, Mass., April 5th–10th, 1959, p. 80-0; *ibid.*, **81**, 1262 (1959); **82**, 2469 (1960).

(5) H. B. Charman and C. K. Ingold, *J. Chem. Soc.*, 2523, 2530 (1959).

(6) R. E. Dessy and Y. K. Lee, *J. Am. Chem. Soc.*, **82**, 689 (1960).

(7) H. Sawatzky and G. Wright, *Can. J. Chem.*, **36**, 1555 (1958).