# **DEOXYMERCURATION**<sup>1</sup>

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## ABSTRACT

The conversion of several stereoisomeric oxymercurials to alkenes (deoxymercuration) has been studied with hydrogen chloride in anhydrous and near-anhydrous methanol. In each instance the addition of water decreases the second-order rate. In benzene the addition of water to the anhydrous system first accelerates and then decreases the reaction rate. These results have been interpreted in support of molecular rather than ionic participation by hydrogen chloride. Since molecular participation requires the  $\uparrow\uparrow$  arrangement of alkoxy and chloromercuri groups for easy reaction it follows that oxymercuration also follows a molecular and not a "mercurinium ion" mechanism in the normal reaction.

The decomposition of 2-oxyorganomercuric salts to mercuric salts and alkenes has been called deoxymercuration (11). It is a much milder reaction than is the scission of simple alkylmercuric salts, some of which resist prolonged heating with strong acids. This difference must be due to the vicinal oxygen linkage. Several opinions have been expressed about the manner in which this oxygen assists the scission of the carbon-mercury link. It will be seen that these opinions are closely related to the ideas of oxymercurial formation. For this reason a decision about the manner in which deoxymercuration occurs ought to specify the mechanism of oxymercuration.

According to Whitmore (20) deoxymercuration is induced by formation of an oxonium salt, I, which then decomposes into an alcohol, an alkene, and a mercuric monocation (where X is an acid substituent bound covalently).



According to this mechanism the rate of deoxymercuration ought to be dependent on the strength of the acid used in the reaction. This dependence on acid strength has been confirmed by experiment (11).

According to another, more recent, opinion the reaction is of the " $E_2$  elimination" type (22) in which an anion is presumed to coordinate with the mercurial (II) to force the



indicated electronic displacement. Presumably the experimental basis for this scheme lies in the early work of Sand and Breest (15) and a recent reconsideration of it (14). However these experiments were inconclusive. Moreover it has been shown (11) that deoxymercuration by hydrogen chloride in methanol is insensitive to addition of sodium chloride or mercuric chloride. Actually no factual proof of the  $E_2$  scheme exists.

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The scheme may have been revived for several reasons. First it is essentially the reversal of a popular mechanism for oxymercuration (9). These authors propose that a mercuric monocation coordinates with an alkene to give an "alkanemercurinium" ion, III, which reacts with an alkoxide ion to yield the oxymercurial, IV.



Secondly, it may be noted that the final reaction of this series involves an inversion (postulated also for the deoxymercuration) from which a *trans*  $(\uparrow\downarrow)$  oxymercurial would be formed. The mechanism received strong support from an X-ray diffraction study (4) in which  $\alpha$ -2-methoxycyclohexylmercuric chloride was assigned the  $\uparrow\downarrow$  configuration. However, it is now realized that this X-ray diffraction study is non-definitive because the ring constellation cannot be discerned adequately in the presence of several heavy atoms. If, instead of the orthodox "crown" ring, the "flexible" cyclohexane ring (8, 7) is assumed, the location of the ring substituents may be a consequence of the ring deformation rather than of substituent configuration. Attempts to refine the structures so as to locate the ring carbon atoms more concisely than in the original study have proved to be fruitless.

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However, the inversion mechanism does account satisfactorily for the experimental observation that in certain circumstances the deoxymercuration is stereospecific. When the single diastereomeric oxymercurial produced from a single geoisomer is treated with concentrated hydrochloric acid the single geoisomer is regenerated without contamination (24). Inspection of the postulated mercurinium ion shows that it will be involved stereospecifically in oxymercuration, as also will the  $E_2$  reaction specified for deoxymercuration. Moreover, the conformation required for the inversion reactions should be more favorable in one diastereomer than in another, and in many instances this difference in reactivity is observed. Thus it remains only to demonstrate that the ionic species significant to these mechanisms actually are available in the reacting systems.

There is evidence against the direct participation of ionic species in the oxymercuration of alkenes. According to these studies (12) the reacting species is a basic mercuric salt which undergoes a four-center addition to the alkene.

 $HgX_2$  and  $ROH \xrightarrow{} ROHgX$  and HX



It may be seen that this mechanism also satisfies the experimental requirement of a

second-order stereospecific reaction but it differs from the ionic inversion mechanism because it involves direct  $(\uparrow\uparrow)$  addition rather than  $\uparrow\downarrow$  addition.

This mechanism, essentially molecular<sup>\*</sup> rather than ionic, has its counterpart in deoxymercuration, where a molecule of hydrochloric acid (X = Cl) is thought to coordinate with the alkene to form a six-atom "quasi-cyclic" intermediate, V. In V the



electronic redistribution causes scission to the products. It may be seen that these explanations that are based on direct rather than inverse addition also imply stereospecificity, either of product or of reaction rate. Actually the direct  $(\uparrow\uparrow)$  explanation fits better the oxymercuration of stilbene and isostilbene and the deoxymercuration of the corresponding two diastereomeric methoxymercurials than does the inverse mechanism (23). However, one essential difference in the two mechanisms involves ion participation in one but not in the other. This criterion has been evaluated in the present report.

The deoxymercurations described above have involved hydrochloric acid. To some, this might seem to involve high ion concentration although it is evident to the experimenter, by the presence of hydrogen chloride in the gas phase above these deoxymercuration systems, that molecular hydrogen chloride must be present. Moreover, the deoxymercurating agents do not need to be strong acids. For example,  $\alpha$ -2-methoxycyclohexylmercuric chloride reacts rapidly in methanol with isopropylmercaptan. Although the  $K_A$  of this mercaptan in water is probably smaller than that of acetic acid (toward which the mercurial is reasonably stable at 25°) the precipitation of chloromercuric isopropylmercaptide is immediate. Steric convenience ought to be involved, and this effect is typified by a quasi-cyclic intermediate like IV in which HX would be isopropylmercaptan.

It is convenient to deoxymercurate in a solution consisting of methanol and concentrated hydrochloric acid but this stereospecific system may contain ionic as well as molecular species. As the water content of the system is decreased, the extent of ionization ought to become minimal. Therefore it is of interest to measure the rate of deoxymercuration in anhydrous and near-anhydrous methanol and this has been done by use of the colorimetric analysis for reacting systems of oxymercurals (3, 12).

The deoxymercurations of  $\alpha$ -2-methoxycyclohexylmercuric halides by the appropriate halogen acids are recorded in Table I. In anhydrous methanol the reaction is second-order and very rapid but the rate is decreased markedly by the addition of a few per cent of water. Comparison of the rate constants shows that the deoxymercuration is relatively insensitive to the halide involved in the reaction although the order of reactivity is roughly paralleled by the dipole moments of the three halides in dioxane solution (2). The  $\beta$ -2methoxycyclohexylmercuric chloride, which should be sterically unfavorable toward deoxymercuration, does indeed react with hydrogen chloride in anhydrous methanol at

\*This term is applied to a substance which acts as a stereochemical unit and therefore will include the category of "ion-pair".

least 100 times slower than the  $\alpha$ -diastereomer even when the concentration is increased 15-fold. However, this slow rate is decreased at least 10-fold by addition of 1% of water.

TABLE I

DEOXYMERCURATION OF $\alpha$ -2-METHOXYCYCLOHEXYLMERCURIC	C HAL	IDES
$(RHgX, 1.0 \times 10^{-3} \text{ mole/liter})$ by hydrogen halides,	HX,	IN
96:4 METHANOL-WATER OR METHANOL AT 25°		

	HX, mole	HX, Medium		
Х	$\overline{\text{liter}} \times 10^{-3}$	CH3OH	H <sub>2</sub> O	mole. sec.
Cl	1.0	100	0	3.53
Cl	1.0	96	4	0.65
Br	0.5	96	4	$0.75^{*}$
Br	1.0	96	4	0.74
Br	2.0	96	4	0.76
I	0.5	96	4	0.72
I	1.0	96	4	0.70
I	2.0	96	4	0.71

\*Rate constants for bromides and iodides are calculated from early stages of the reaction; the rate decays slightly in later stages.

A similar effect is observed during the deoxymercuration of either of the diastereomeric 2-methoxy-1,2-diphenylethylmercuric chlorides. The  $\beta$ -diastereomer (derived from *trans*stilbene) in anhydrous methanol follows rapid second-order kinetics (k = 2.1 liters mole<sup>-1</sup> sec. $^{-1}$ ) and is 80% complete within an hour. Fig. 1 shows that this rate, determined by analysis after 45 minutes of reaction time, is decreased according to the amount of water present in the methanol. The  $\alpha$ -diastereomer (derived from *cis*-stilbene) is deoxymercurated more slowly, and it is necessary to use methanol solutions four times as strong as those 0.001 molar in mercurial and in hydrogen chloride which were used for the reaction with the  $\beta$ -diastereomer. Fig. 2 shows that the deoxymercuration rate of the  $\alpha$ -diastereomer also decreases with increasing amounts of water in the methanol. It may be of interest that the rate is essentially constant when more than 6% of water is present. This

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FIG. 1. Effect of water on the amount of deoxymercuration of  $\beta$ -1-chloromercuri-2-methoxy-1,2-diphenyl-ethane during 45 minutes at 25°. [HCl] = [mercurial] = 0.001 mole/liter. FIG. 2. Effect of water on the amount of deoxymercuration of  $\alpha$ -1-chloromercuri-2-methoxy-1,2-di-phenylethane during 60 minutes at 25°. [HCl] = [mercurial] = 0.004 mole/liter.

level is about the same as that reported for the minimum in limiting equivalent conductance for hydrogen chloride in aqueous methanol (16).

The following set of equations describe the chemistry which thus far has been reported here:

$$MeOH + HX \rightleftharpoons MeOH_2^{\oplus} + X^{\Theta}$$
[1]

$$MeOH_{2}^{\oplus} + MeO - \bigcup_{l}^{l} - \bigcup_{l}^{l} - HgX \rightleftharpoons MeO - \bigcup_{l}^{l} - \bigcup_{l}^{l} - HgX^{\oplus} + MeOH$$

$$H$$

$$(2)$$

н

$$\overset{\uparrow}{\text{MeOCH}_2\text{CH}_2\text{Hg}X^{\oplus} \to \text{MeOH} + \overset{\downarrow}{\text{C}==} \overset{\downarrow}{\text{C}} + \text{Hg}X^{\oplus}$$
(3)

$$H_2O + HX \rightleftharpoons H_3O^{\oplus} + X^{\ominus}$$
<sup>[4]</sup>

$$MeOH_{2}^{\oplus} + H_{2}O \rightleftharpoons H_{3}O^{\oplus} + MeOH$$

$$[5]$$

$$H_{3}O^{\oplus} + MeO - C - C - HgX \rightarrow MeO - C - C - HgX^{\oplus} + H_{2}O$$
[6]

$$HX + MeO - C - HgX \rightleftharpoons MeO - C - C - HgX \qquad [7]$$

$$MeO - C - C - HgX \rightarrow MeOH + C = C + HgX_2$$
[8]

Among these, equations [1], [2], [3], [7], and [8] represent reactions in anhydrous media, while [4], [5], and [6] represent reactions in which water is present. Since the addition of water decreases the rates of deoxymercuration by hydrogen chloride that are described in the report, it is doubtful that equation [6] is significant to these reactions. On the other hand the diminution of molecular hydrogen chloride by increasing amounts of water according to equation [4] would account for the decreasing rate of deoxymercuration in this circumstance if equations [7] and [8] are valid. The expectation conforms with the observation of Shedlovsky and Kay (16) that the ionization of hydrogen chloride seems to decrease as the alcohol content of methanol-water systems increases.

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The numerical data of this latter paper (16) indicate that  $10^{-3}$  molar solution should contain slightly more than 1 mole per cent of molecular or ion-pair hydrogen chloride. Reaction according to the equations [7] and [8] is thus plausible. However, the experimental results may also be explained in terms of equations [1], [2], and [3], assuming that the concentration of methoxonium ion is reduced by addition of water according to equation [5]. Actually the paucity of information respecting the true composition of the methanol – hydrogen chloride system makes a choice between the two mechanisms relatively meaningless except insofar as the results may be compared with those in a solvent of lower dielectric constant.

We have chosen to use benzene for this comparison. For our studies in this solvent we have considered the following additional equations:

$$2\mathrm{HX} \rightleftharpoons (\mathrm{HX})_2$$
 [9]

$$C_6H_6 + HX \rightleftharpoons C_6H_7^{\oplus} + X^{\ominus}$$
[10]

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$$C_{6}H_{7}^{\oplus} + MeO - \stackrel{I}{C} - \stackrel{H}{C} HgX \rightleftharpoons MeO - \stackrel{I}{C} - \stackrel{H}{C} HgX \rightleftharpoons + C_{6}H_{6}$$
[11]

It is evident from equations [1]–[11] inclusive that the use of benzene includes the complication that methanol is released as one of the products. Partly for this reason the kinetic data are not very reproducible and only the first stages of the reaction give useful data. The rate constants calculated from these data may be expected to be in error on the low rather than on the high side because of inadvertent admission of water vapor, even though atmospheric contamination was avoided vigorously.

According to electrical polarization studies (17) with hydrogen halides in benzene there seems to be no evidence for the phenyl cation. If it exists at all the concentration must be extremely low. Deoxymercuration in benzene via the phenyl cation ought therefore to be inordinately slow. Moreover, an initially slow rate ought to be enhanced if the reaction proceeds by an ionic mechanism because of methanol which appears as a product. Actually the rate constant for deoxymercuration of  $\alpha$ -2-methoxycyclohexylmercuric chloride in anhydrous benzene (described below) is greater than that in anhydrous methanol; also there is no indication of autocatalysis.

The reaction of  $\alpha$ -2-methoxycyclohexylmercuric chloride in anhydrous benzene is too fast for convenience, and solutions not stronger than  $2.0 \times 10^{-4}$  molar in mercurial and hydrogen chloride must be used in order to follow the reaction kinetically. Because of analytical difficulties prior to the actual colorimetric reading and because of hygroscopicity the numerical value of the second-order rate constant (5.6 liters mole<sup>-1</sup> sec.<sup>-1</sup> at this low concentration is uncertain. However a comparison of this slope (A, Fig. 3) with B (2.2 liters mole<sup>-1</sup> sec.<sup>-1</sup>) and C (1.6 liters moles<sup>-1</sup> sec.<sup>-1</sup>) in which approximately  $3 \times 10^{-3}$  mole liter<sup>-1</sup> of water is included with the benzene shows that this deoxymercuration is strongly inhibited by water.



FIG. 3. Second-order rate constants (25°), deoxymercuration in benzene, anhydrous (O) or containing about  $3 \times 10^{-3}$  mole/liter water ( $\Phi$ ,  $\Phi$ ).

According to this behavior deoxymercuration in benzene does not involve freely-mobile ions which can enter into second-order rate processes. On the other hand, the alternative to a free ionic agent is not simple. Perhaps it should not be expected to be simple. The enhanced electric moment of hydrogen chloride in benzene over the moment in the gaseous state indicates association of the halide with the solvent (17), and self-association together with the solvent is not rigorously excluded. Indeed Beckmann and Lockemann in their classical study (1) show that hydrogen chloride seems to associate in anhydrous benzene and that the extent of association (1.75–2.79) decreases (to 1.16) as very small amounts

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of water are added progressively. Therefore evidence for equation [9] exists and seems to be involved in deoxymercuration studies with the two 2-methoxy-1,2-diphenylethyl-mercuric chloride diastereomers.

The  $\beta$ -diastereomer of 2-methoxy-1,2-diphenylethylmercuric chloride reacts more slowly with hydrogen chloride in benzene than does  $\alpha$ -methoxycyclohexylmercuric chloride, so solutions  $1.5-2.0 \times 10^{-3}$  molar in the stilbene mercurial and in hydrogen chloride may be used. Although this deoxymercuration is thus easier to study in respect of water content it is, unfortunately, subject to strong catalytic acceleration by mercurous chloride. Since this  $\beta$ -mercurial tends spontaneously (especially in light) to decompose into mercurous chloride, and also because of the catalytic effect of liberated methanol, the reactions may be studied only qualitatively. Fig. 4 shows that the rate is decreased by





F16. 5. Deoxymercuration at 25° of  $\beta$ -2-methoxy-1,2-diphenylethylmercuric chloride  $2.0 \times 10^{-3}$  molar in benzene.

addition to the anhydrous system  $(2 \times 10^{-3} \text{ molar in mercurial and acid})$  of a molar excess of water. On the other hand the addition of less than a molar equivalent of water to the anhydrous system causes an increase in rate. The latter behavior is shown in Fig. 5. This diagram includes also an example of the accelerating effect of mercurous chloride, which we shall not now attempt to explain. However, with respect to water it seems reasonable to suggest that the enhancement of rate by addition of 0.75 equivalent involves the reversal according to equation [9] of the association observed by Beckmann and Lockemann, while the decreased rate with one or more equivalents of water is caused by loss of molecular hydrogen chloride because of ionization according to equation [4].

The effect of water in benzene has also been studied in the deoxymercuration of  $\alpha$ -2methoxy-1,2-diphenylethylmercuric chloride by hydrogen chloride. In this instance the analytical method is a manometric one depending on diminution of the vapor pressure of hydrogen chloride as it is consumed in the reaction. The record (Fig. 6) of an experiment in anhydrous benzene versus a benzene solution containing less than one molar equivalent of water shows its accelerating effect to be similar to that observed for the  $\beta$ -diastereomer. Not shown is a curve demonstrating that mercurous chloride also accelerates the deoxymercuration of the  $\alpha$ -diastereomer.

In summary it would seem that if deoxymercuration is faster in benzene than in methanol, if common ion effects are not found in the latter medium, and if the retarding

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FIG. 6. Manometric analysis, deoxymercuration at  $25^{\circ}$  of  $\alpha$ -2-methoxy-1,2-diphenylethylmercuric chloride 0.01 molar by hydrogen chloride 0.01 molar.

effect of water is comparable in both media, then the improbability of an ionic mechanism in benzene renders improbable an ionic mechanism for all of these stereospecific deoxymercurations. However, it remains to prove that the reaction in benzene is as stereospecific as it is in methanol. This similarity has now been established by isolation of *cis*stilbene uncontaminated by the *trans* isomer when  $\alpha$ -2-methoxy-1,2-diphenylethylmercuric chloride is treated with one equivalent of hydrogen chloride in benzene.

It should be noted that the non-ionic deoxymercuration is specified only for the stereospecific reactions. Actually we have succeeded in producing a few per cent of *trans*-stilbene from the  $\alpha$ -diastereomer by treatment with a 1:1 mixture of concentrated hydrochloric acid in methanol. Of course we cannot attribute the slight non-stereospecificity to an ionic deoxymercuration because *cis*-stilbene might have been the initial product which then was isomerized by the acidic medium. But also the non-stereospecificity may be due to the ionic reaction specified by Whitmore.

Such an ionic reaction may also apply to the very slow deoxymercurations of some  $\beta$ -oxymercurials in which the configuration is unfavorable to a quasi-cyclic transition state. Likewise it may apply to deoxymercurations by acids other than the hydrogen halides. But it does not apply to the deoxymercuration which has the same stereospecific behavior as does the corresponding oxymercuration. Both of these processes seem to involve molecular reactants. Therefore both should require *cis* ( $\uparrow\uparrow$ ) configuration in the mercurial. It follows that the "inversion" mechanism is not adequate to describe either oxymercuration or deoxymercuration, in respect of alkenes such as are considered in this report.

## EXPERIMENTAL\*

## $\alpha$ -2-Isopropoxycyclohexylmercuric Chloride

To a solution of 3.18 g. (0.01 mole) of mercuric acetate in 30 ml. of propanol-2 was added 0.90 g. (0.011 mole) of cyclohexene. After 3 hours, filtration into 25 ml. of 5% aqueous sodium chloride at 0° C. precipitated 3.05 g. (80%) of the isopropoxymercurial, m.p. 90.5–91.5° C. Crystallization from absolute ethanol (20 ml./g.) raised the melting point to 94.8–95.5° C. Calc. for  $C_9H_{17}ClHgO$ : C, 28.7; H, 4.52; Hg, 53.2. Found: C, 28.4; H, 4.68; Hg, 52.2.

\*Melting points have been corrected against reliable standards. X-Ray diffraction data have been obtained with  $C_{\rm U} \ K_{\alpha}$  (Ni filtered) radiation at d spacings in A at visual relative intensities  $I/I_1$ .

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## $\alpha$ -2-Alkoxycyclohexylmercuric Halides Used in Kinetic Studies

These oxymercurials, prepared by standard procedures, were purified to melt as shown in Table II.

Diastereomer	R	X	M.p., ° C.	Reference
α	Me	Cl	115.2-116.0	(25)
β	Me	Cl	114.1 - 114.5	(24)
α	Et	CI	60.8-61.5	(5)
α	Pr	CI	57.5 - 58.5	(12)
α	t-Bu	Cl	115.0 - 116.0	(5)
ά	$MeOC_{2}H_{4}$	CI	121.5 - 122.5	(12)
α	Н	Cl	153.0 - 153.6	(5)
α	Me	Br	114.0 - 114.5	(13)
α	Me	I	81.4 - 82.0	(6)

TABLE II						
Ielting	POINTS	OF	2-ALKOXYCYCLOHEXYLMERCURIC	HALIDES,	ROC <sub>6</sub> H <sub>10</sub> HgX	

## Deoxymercuration Using Benzoyl Chloride

A. With  $\alpha$ -2-Methoxy-1,2-diphenylethylmercuric Chloride

To 1.12 g. (0.0025 mole) of this mercurial in 15 ml. of ethanol-free anhydrous chloroform was added 0.29 ml. (0.0025 mole) of freshly distilled benzoyl chloride, b.p. 197° C. After 96 hours, 0.66 g. (97%) of mercuric chloride was filtered off. Vacuum evaporation of the filtrate left 0.80 g. of oil with the odor of methyl benzoate. It was refluxed with 20 ml. of 10% aqueous sodium hydroxide for 270 minutes, then steam-distilled. Etherous extraction (45 ml.) of the distillate removed 0.42 g. of cis-stilbene (89%), m.p. 3.5-6.0° C. This geoisomer (0.0022 mole) was characterized by treatment with 0.70 g. (0.0022 mole)of mercuric acetate in 15 ml. of anhydrous methanol for 5 hours, followed by filtration into 25 ml. of 10% aqueous sodium chloride. A mixture melting point of the precipitate  $(0.85 \text{ g.}, 70\%, \text{m.p. } 142.5-143.5^{\circ} \text{ C.})$  with  $\alpha$ -methoxydiphenylethylmercuric chloride was not lowered.

## B. With $\beta$ -2-Methoxy-1,2-diphenylethylmercuric Chloride

To 2.24 g. (0.005 mole) of this mercurial in 25 ml. of ethanol-free chloroform was added 0.58 ml. (0.005 ml.) of freshly-distilled benzoyl chloride, b.p. 197° C. After 1 day 1.34 g. (98%) of mercuric chloride was filtered off. Vacuum evaporation of the filtrate left a semisolid oil (1.55 g). This was crystallized from 8 ml. of ethanol, 0.71 g. (79%) of transstilbene, m.p. 122.5-124° C., authenticated by mixture melting point.

## C. With $\alpha$ -2-Methoxycyclohexylmercuric Chloride

To 3.49 g. (0.01 mole) of this mercurial in 25 ml. of ethanol-free chloroform was added 1.40 g. (0.01 mole) of freshly-distilled benzoyl chloride. After 18 hours, 2.58 g. (95%) of mercuric chloride was filtered off. Vacuum evaporation of the solvent left an oil which was extracted with water. The oil, 1.35 g. (99%), was then distilled at 196–198° C. This methyl benzoate (1.10 g., 81%) was characterized by saponification; acidification precipitated 0.78 g. (87%) of benzoic acid, authenticated by mixture melting point.

The use of benzoyl chloride rather than gaseous hydrogen chloride is a convenient variation for stereospecific deoxymercuration. However, there is evidence (by Mr. Paul Chu) that the reaction is not a simple one; indeed it is catalyzed by mercuric chloride, which may be present in trace amounts in the chloromercurials. In relation to the catalytic action it is of interest that the solubility of mercuric chloride in chloroform is enhanced by the presence of an organochloromercurial which is dissolved in the chloroform.

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# Deoxymercuration Using Hydrogen Chloride with $\alpha$ -2-Methoxy-1,2-diphenylethylmercuric Chloride

## A. In Anhydrous Benzene

To 4.47 g. (0.01 mole) of mercurial in a 250-ml. distilling flask was added 60 ml. of a 0.195 N (0.012 mole) solution of hydrogen chloride in benzene during 3 minutes. Mercuric chloride was deposited during this addition; evidently reaction is rapid. After 7 minutes more the solvent was vacuum-evaporated with swirling at 25° C. In a short time the solvent was gone and the residue was quickly treated with excess of 10% aqueous alkali. The *cis*-stilbene was taken up by five washings with ether. The extract, dried by potassium carbonate, was evaporated, 1.62 g., and distilled, b.p. 140–142° C. (14 mm.),  $n_D^{20}$  1.6217, 1.51 g. (84%), leaving no *trans*-stilbene.

## B. In Aqueous Methanol

The same amount of mercurial was stirred 12 hours at 25° C. in 90 ml. of methanol plus 90 ml. of concentrated hydrochloric acid. The system, containing oil droplets, was diluted to 700 ml. with water and thrice extracted with 90-ml. lots of ether. The extract, dried by calcium chloride, was vacuum-evaporated, and the residue chromatographed from commercial hexane on a 12 cm. by 0.8 cm. alumina column (activated at 450° C.). After 90 ml. of eluate the column was extruded, the *trans*-stilbene located by permanganate streak, and removed from the zone by ether. Evaporation left 10 mg. of *trans*-stilbene, m.m.p. 120-122° C., authenticated by mixture melting point. The column eluate yielded 1.37 g. of *cis*-stilbene, which was reconverted to the  $\alpha$ -mercurial, crude m.p. 143-144° C.

## Chloromercuric Isopropylmercaptide

To a solution of 2.85 g. (0.008 mole) of  $\alpha$ -2-methoxycyclohexylmercuric chloride in 60 ml. of methanol was added 0.99 g. (0.013 mole) of isopropylmercaptan. A voluminous white precipitate formed immediately. It was filtered off, washed with methanol (30 ml.), and then with ether (60 ml.), 3.11 g. (100%) of infusible chloromercuric isopropylmercaptide. Calc. for C<sub>3</sub>H<sub>7</sub>ClHgS: C, 11.6; H, 2.25. Found: C, 12.1; H, 2.41.

Identical results were obtained with ethylmercaptan. This compound was regenerated by acidification of the infusible precipitate with hydrochloric acid.

## Kinetic Measurements

These were carried out at  $25.0^{\circ} \pm 0.1^{\circ}$ C.

A. Reagents

The methanol was purified under nitrogen by Lund and Bjerrum's method (10) to be peroxide-free (TiCl<sub>3</sub>) and aldehyde-free (Schiff reagent). The benzene, purified by refluxing and distillation from sodium under nitrogen, was anhydrous and peroxide-free according to test with sodium benzophenone ketyl. The hydrogen chloride and hydrogen bromide were dried by passage through concentrated sulphuric acid and then through anhydrous aluminum chloride. The diphenylthiocarbazone (dithizone) was purified by the method of Winkler (21, 18).

## B. The Apparatus Used for Anhydrous Reactions

The essential pieces of apparatus are shown as the storage burette in Fig. 7 and the reaction flask in Fig. 8. The storage burette, after thorough drying in a nitrogen stream, is filled with 160 ml. of benzene in the tubular absorber  $(195 \times 20 \text{ mm. with fritted glass})$  disperser) and the spherical chamber (68 mm. diameter) above it to a level just below the inlet from the top stopcock. Then hydrogen chloride is passed in through the horizontally-projecting conical joint by distillation (using a dry-ice bath as a source of heat) from a

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FIG. 7. The storage burette for hydrogen chloride in benzene or methanol.



FIG. 8. The deoxymercuration vessel for kinetic studies.

trap in which the acid has been condensed by use of liquid air. When the top stopcock is closed and the three-way stopcock at the bottom of the burette is open hydrogen chloride will pass through the benzene. Finally after 30 minutes sufficient acid has been absorbed. The inlet spiral is immersed in a liquid air bath while the source of hydrogen chloride is

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removed, the three-way stopcock having been closed. The latter is now reopened while a stream of dry nitrogen is passed through the horizontal inlet tube (the top stopcock being open) in order to sweep excess hydrogen chloride away from the area above the benzene solution. Then, all stopcocks being closed, the apparatus is tilted to transfer 100 ml. of the benzene solution into the storage reservoir  $(155 \times 38 \text{ mm.})$  whence it may be standardized in the 10 ml. microburette by sample withdrawal from the plain outlet at the three-way stopcock. During all these operations the vents from the apparatus are protected from moisture by means of connections with U-tubes immersed in liquid air. All interchangeable joints are graphite-lubricated.

The reaction flask (Fig. 8) is constructed with an attachment joint to the burette, a second joint through which the solid mercurial sample is introduced by tipping from a hollow interchangeable stopper at the appropriate time, a dry-gas inlet tube and a capillary stopcock-closed outlet tube from the bottom. With these attachments the vessel does not need to be removed from the thermostat during reaction, the samples being withdrawn by rubber bulb inlet pressure which forces them out via the capillary stopcock into a cup. A definite aliquot is then withdrawn by pipette from the cup. The subsequent colorimetric procedure has been described previously (3, 12). Further detail is available in Mr. Berg's M. A. thesis.

## C. The Manometric Apparatus

A differential manometer of the Warburg (19) type was modified by addition of an interconnecting stopcock between the reaction side and the compensator side in order to equilibrate the gas phase before the sample tube containing solid mercurial was inverted into the benzene – hydrogen chloride solution. Transferral of this solution to reaction and compensator flask from its preparative source (essentially the burette and reaction flask described above) was accomplished through serum caps via a hypodermic syringe.

D. Effect of Water in Methanol on Deoxymercuration

Into each of six 10 ml. volumetric flasks containing either 0, 0.2, 0.4, 0.6, 0.8, or 1.0 ml. of water was added 0.52 ml. of anhydrous methanol which was 0.0194 N in hydrogen chloride. Then 2 ml. of 0.005 M of mercurial in anhydrous methanol was added and the flask was filled quickly to volume with methanol. After brief shaking the flask was held at 20° for 5 minutes, then 1 ml. was rapidly diluted to 100 ml. with water. Ten milliliters of the diluate was thrice extracted at once by 5 ml. portions of chloroform, then 5 ml. of the aqueous layer was analyzed colorimetrically. The percentages of deoxymercuration of  $\beta$ -1-chloromercuri-2-methoxy-1,2-diphenylethane with increasing additions of water were 83.6, 59.5, 46.3, 36.7, 30.1, and 27.2. The corresponding percentages for the  $\alpha$ diastereomer were 36.7, 10.7, 7.7, 5.2, 5.2, 5.2.

#### REFERENCES

- BECKMANN, E. and LOCKEMANN, G. Z. physik. Cl BROOK, A. G., DONOVAN, R., and WRIGHT, G. F. Z. physik. Chem. 60, 385 (1907).
- Can. J. Chem. 31, 536 (1953).
- BROOK, A. G., RODGMAN, A., and WRIGHT, G. F. BROOK, A. G. and WRIGHT, G. F. Acta Cryst. 4 J. Org. Chem. 17, 988 (1952).
- Acta Cryst. 4, 50 (1951)
- Can. J. Research, B, 28, 623 (1950). BROOK, A. G. and WRIGHT, G. F.
- J. Am. Chem. Soc. 72, 3821 (1950). BROOK, A. G. and WRIGHT, G. F. 6, GEORGE, M. V. and WRIGHT, G. F.
- Can. J. Chem. **36**, 189 (1958). J. Am. Chem. Soc. **78**, 3369 (1956). KUMLER, W. D. and HUITRIC, A.
- KUMLER, W. D. and HUITRIC, A. J. Am. Chem. Soc. **78**, 3369 (1956). LUCAS, H. J., HEPNER, F. R., and WINSTEIN, S. J. Am. Chem. Soc. **61**, 3102 LUND. H. and BJERRUM, J. Ber. **64**, 210 (1931). RODGMAN, A., SHEARER, D., and WRIGHT, G. F. Can. J. Chem. **35**, 1377 (19, RODGMAN, A. and WRIGHT, G. F. J. Org. Chem. **18**, 1617 (1953). ROMEYN, J. and WRIGHT, G. F. J. Am. Chem. Soc. **69**, 697 (1947). ROWLAND, R. L. and KLUCHESKY, E. F. J. Am. Chem. Soc. **73**, 5490 (1951). J. Am. Chem. Soc. 61, 3102 (1939).
  - 10.
- Can. J. Chem. 35, 1377 (1957). 11.
- 12.
- 13.
- 14.

- SAND, J. and BREEST, F. Z. physik. Chem. 59, 424 (1907).
   SHEDLOVSKY, T. and KAY, R. L. J. Phys. Chem. 60, 151 (1956).
   SMITH, J. W. Electric dipole moments. Butterworths Scientific Publications, London. 1955. p. 314.
   STONESTREET, G. and WRIGHT, G. F. Can. J. Research, B, 18, 246 (1940).
   WARBURG, O. Biochem. Z. 152, 51 (1924).
   WHITMORE, F. C. Chem. Eng. News, 26, 668 (1948).
   WINKLER, W. O. J. Assoc. Official Agr. Chemists, 18, 638 (1935).
   WINSTEIN, S., TRAVLOR, T. G., and GARNER, C. S. J. Am. Chem. Soc. 77, 3741 (1955).
   WRIGHT, G. F. Can. J. Chem. 30, 268 (1952).
   WRIGHT, G. F. J. Am. Chem. Soc. 57, 1993 (1935).