Silica.—The silica used was Holmes' chalky silica gel prepared in the Severance Laboratory.

"Hyflo Super Cel."—A siliceous earth with practically no adsorbent qualities, purchased from Johns-Manville, Cleveland.

Nitrogen.—Compressed gas, from the Ohio Chemical Co., Cleveland, containing less than 0.05% oxygen. This trace of oxygen was removed by passing the gas through alkaline pyrogallol.

Methods

Our columns were set up according to the diagram in Fig. 2. The tip of the column tube was tightly plugged with glass wool and the entire system was then filled with nitrogen. A thin mixture of activated carbon and pentane, well shaken, was then poured into the column and allowed to settle. While the level of the liquid fell to the upper level of the column of carbon the tube was tapped with a block of wood to dislodge gas bubbles. A pentane solution of the concentrate was then carefully added and allowed to filter down through the carbon with the aid of slight suction at B, while nitrogen entered the top of the column at A. After all the solution of concentrate had entered the carbon, pentane was carefully added through the separatory funnel and allowed to wash the concentrate down through the carbon. Fractions of the filtrate of from 50 to 150 cc. each were collected. Upon changing receivers, stopcocks B and C at the bottom were closed (cutting off suction), B was opened to admit nitrogen to the partially evacuated receiver before removal, and a clean nitrogen-filled bottle was connected.

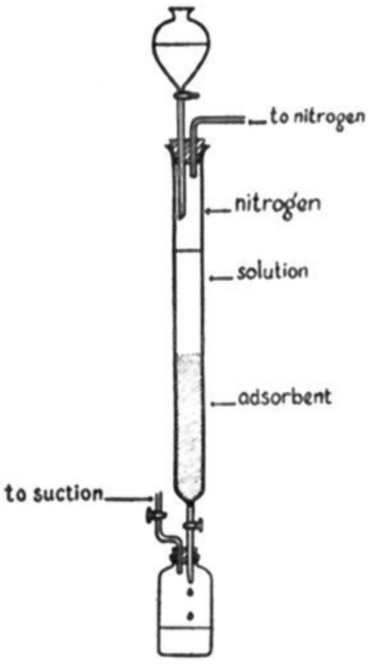


Fig. 2.—Column for selective adsorption.

Only slight suction can be used, otherwise the powdered adsorbent packs too tightly for effective filtration. To aid in hastening the filtration through magnesia columns we used a heat-treated siliceous earth, "Hyflo Super Cel," mixed in equal part by weight with the magnesia as suggested by Strain in his work on carotenes. This siliceous earth is a poor adsorbent but aids in more uniform packing of the magnesia and in more rapid filtration. Both powders were activated together (after thorough mixing) in order to remove any moisture or oxygen present.

Our usual practice was to filter about 6 g. of concentrate, contained in 50 cc. of pentane solution, through a column of carbon 2.5 cm. in diameter and 23 cm. high (about 40 g. of carbon). The filtrate from a column of this size contained from 1 to 40 mg. per cc.

Summary

1. Cholesterol and some other impurities were frozen out of a pentane solution of the nonsaponifiable portion of halibut-liver oil; the resulting solution was then fractionated by Tswett adsorption columns with an improved technique. Using a column of a specially prepared oxygen-free carbon followed by treatment with a column of a new type magnesia a concentrate of vitamin A at least 40% more potent than any previously recorded was obtained.

2. Lovibond tintometer readings were checked biologically and spectrographically in the Parke-Davis laboratories and elsewhere.

3. The most potent concentrate had a blue value of at least 140,000.

OBERLIN, OHIO RECEIVED JULY 16, 1935

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Mercuration of Ethylenes and Reactions of the Methoxy Mercurials

BY GEORGE F. WRIGHT[1]

Introduction

When an unsaturated compound is treated with mercuric acetate in alcohol solution, the elements of methoxymercuric acetate combine with the ethylene. The nature of the product has been the subject of controversy for some years and the evidence has been well summarized by Adams, Roman and Sperry.[2] These authors as well as others[3,4] have rejected Manchot's hypothesis[5] that such mercurials are molecular compounds of the type $RCH{=}CHR'\cdot R''OHgX$ (I) and they have preferred the second of two mechanisms of formation which designate the reaction as ordinary addition to a double bond. More recent work has substantiated the structure for the mercurials as III rather than I. Marvel and co-workers,[6] by separating disastereomers with different rotations from the mercuration of optically active cinnamic esters, have shown that

---

[1] National Research Fellow in Chemistry.

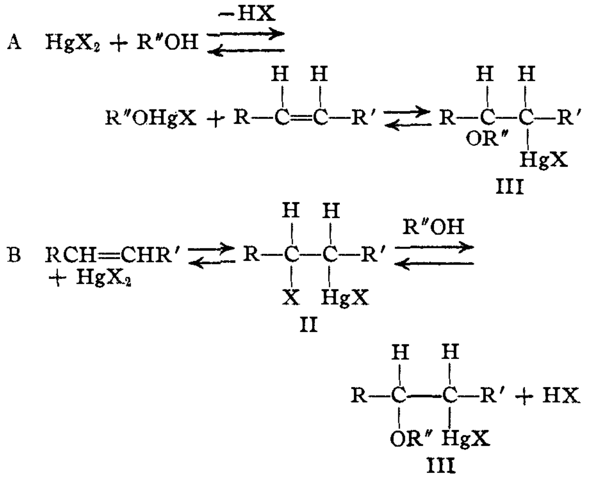
[2] Adams, Roman and Sperry, THIS JOURNAL, **44**, 1781 (1922).

[3] Mills and Adams, *ibid.*, **45**, 1842 (1923).

[4] Middleton, *ibid.*, **45**, 2763 (1923).

[5] Manchot, *Ann.*, **420**, 174 (1920); *ibid.*, **421**, 316, 331 (1921).

[6] Sandborn and Marvel, THIS JOURNAL, **48**, 1409 (1926); Griffith and Marvel, *ibid.*, **53**, 789 (1931).



asymmetric centers are actually produced in the synthesis. Likewise the instability of the mercurials finds a parallel in the analogous organomagnesium compounds,[7] which exhibit the same tendency to decompose into the unsaturated compound and the alkoxy metal salt.

This communication is concerned with further proof for the existence of structure III as well as a critical study of its mode of formation. To this end the methoxymercurials have been prepared from *cis* and *trans* methyl cinnamate, isostilbene, styrene, propenylbenzene, cyclohexene and 1-phenylbutadiene-1,3. In general their properties are identical with those of analogous mercurials already known. Specifically the rates of formation as well as the type differences intrinsic in the ethylenes used indicate that the first of the alternative mechanisms suggested by Adams, Roman and Sperry actually takes place. This disposes of an obnoxious feature of mechanism B, namely, the formation of the ether III from the ester II at a carbon atom which would not be expected to enhance the tendency toward this limited reaction. This tendency should be greater when such a carbon atom is surrounded with increased unsaturation; the greater ease of mercuration found with styrene and cyclohexene as compared with methyl cinnamate and isostilbene suggest that this etherification is at least not the controlling step in the reaction.

Furthermore, a kinetic study of *cis* methyl cinnamate mercuration at varied concentrations indicates that the reaction is second order. The results are complicated by the existence of a measurable equilibrium, demonstrated in the cases of methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate and α-acetoxymercuri-β-methoxy-β-phenylethane; nevertheless, the agreement among the second order constants leaves little doubt that the rate-controlling reaction is bimolecular. Such an order militates against mechanism B, where the etherification involved in the second step should be pseudo-unimolecular, especially in the higher dilutions.

The question arises whether the formation of II in the first step of mechanism B might not control the rate and thus explain the second order constants. It is undeniable that addition products of unhydrolyzed mercuric salts to ethylenes do exist,[8] either as type II or as the molecular compound $RCH=CHR'\cdot HgX_2$ (IV). However, Hugel and Hibou have observed that addition compounds of type II are formed in a few minutes. With the exception of the styrene reaction, none of the methoxy mercurials (Type III) is formed so rapidly. Furthermore, if formation of II were the rate-controlling step the choice of alcohol used as reactant should have relatively little effect upon the reaction velocity whereas, in point of fact, the mercuration proceeds slowly in water but is much more rapid in methanol, although progressively slower when higher alcohols are employed.[9] It is, then, unlikely that the second order constants are a result of the reactions involving mechanism B.

Mechanism A is supported by several innovations in the reaction. First, the addition of a small amount of nitrate ion markedly accelerates the process. This would be expected if hydrolysis of mercuric salt were a prerequisite to formation of III.[10] Second, the addition of sodium methylate (necessarily toward the end of the reaction to avoid precipitation of mercuric oxide) soon carries the reaction to completion. This latter modification, to be sure, does not differentiate between mechanisms A and B. Its action becomes more understandable when addition of an equivalent of acetic acid to a methanol solution of the acetoxymercurial is found not to shift the equilibrium. Likewise when cyclohexene is treated with methoxymercuric chloride, prepared by interaction of equivalent amounts of sodium methylate and mercuric chloride, the product, 1-chloromercuri-2-methoxycyclohexane,

---

[7] Tallman, This Journal, **56**, 126 (1934).

[8] Hugel and Hibou, *Chimie et Industrie*, Special No., 296 (Feb., 1929) [*C. A.*, **23**, 3898 (1929)].

[9] Schoeller, Schrauth and Struensee, *Ber.*, **43**, 695 (1910).

[10] Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Company, New York City, 1923, Vol. IV, p. 991.

is difficult to explain on any basis other than mechanism A. Unfortunately for a good case, the formation of intermediates like type II or IV can also be demonstrated. Thus, if styrene in an inert solvent is treated with mercuric acetate for some hours and the solvent and excess of styrene are removed, the residue when treated with methanol is converted to α-acetoxymercuri-β-methoxy-β-phenylethane. When this method is applied to cyclohexene the mercurial does not form. Although the reaction with styrene may be misleading because of difficulty in extracting the excess of reactant, the significant yield indicates that the intermediate does form. There is, however, no good reason to assume that the styrene intermediate reacts *per se* rather than in its dissociation fragments, styrene and mercuric acetate.

There is, of course, the possibility that in methanol solution methoxymercuric acetate exists as methoxy and acetomercury ions which add at random to the double bond. This should give rise to a mixture of diastereomers, whereas each mercurial actually produced is a chemical individual. Furthermore, when *cis* and *trans* methyl cinnamates are mercurated the isomeric racemic forms are obtained, respectively. On the basis of random addition the pure compounds obtained would not be expected. The fact that methyl *cis* cinnamate reacts about three times as fast as the *trans* isomer,[11] as shown by the relative half-lives (Fig. 1), likewise indicates that the addition proceeds by way of the undissociated methoxymercuric acetate, for the space configuration should offer but little hindrance to the ions. In the case of the geoisomeric stilbenes this is even more apparent since the *trans* stilbene does not react at all, although a good yield of mercurial is obtained from the *cis* isomer (isostilbene). It is in keeping with this concept that nitrate ion (assumed only to promote alcoholysis) does not cause *trans* stilbene to mercurate.

On the basis of this evidence it is believed that formation of the α-methoxy mercurials proceeds *via* mechanism A, as a result of the tendency of mercuric salts to hydrolyze or alcoholize in an appropriate medium.

Since the methoxy mercurials are stable toward aqueous alkali, it has been customary to consider the mercuration complete when this reagent no longer precipitates mercuric oxide. This test has been found to be unreliable and quite misleading. The disappearance of mercuric ion may coincide, as in the case of the rapid reaction with styrene, with completion of the formation of III, but in the greater number of cases the reaction is not finished when the mercuric ion disappears. This discrepancy between removal of mercuric ion and the end of the reaction is illustrated in Fig. 1, the notation Hg indicating the time at which no mercuric ion is detectable. Such a test is evidently not an absolute criterion of completion of reaction.

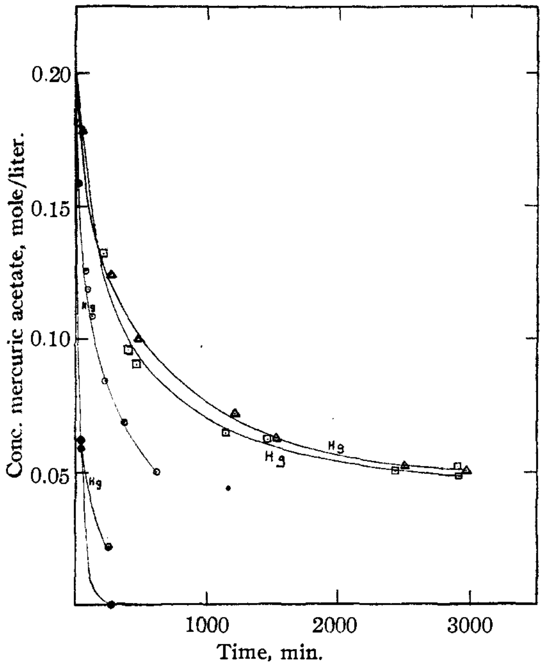


Fig. 1.—△, Isostilbene; ☐, *trans* methylcinnamate; ○, *cis* methylcinnamate; ◒, *trans* methylcinnamate + nitrate ion; ●, isostilbene + nitrate ion.

Reports concerning the instability of these mercurials have not been exaggerated. In addition to the ease of acid splitting, they decompose thermally to regenerate the unsaturated compounds. This has been shown in the case of *meso* and *dl* methyl α-chloromercuri-β-methoxy-β-phenylpropionate, the decomposition temperatures being 159 and 170°, respectively. In both cases *trans* methyl cinnamate is the sole product.

When methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate is treated with alcoholic ammonium sulfide, the acetoxymercuri group is replaced by hydrogen and methyl β-methoxy-β-phenylpropionate is produced.[12] It has been

---

[11] This is in agreement with selective mercuration of the cinnamic acids, Biilmann, *Ber.*, **35**, 2571 (1902).

[12] Schoeller, Schrauth and Struensee, *ibid.*, **44**, 1432 (1911).

found that hydrogen sulfide in alcoholic pyridine, also aqueous sodium thiosulfate, is equally efficient in this transformation. The reaction appears to be limited to acids and esters, since every other mercurial tried yielded only the parent ethylene. In the case of the styrene mercurial, using sodium thiosulfate there was evidence for the transient existence of either the thiosulfate mercurial[3] or the *bis*-mercurial but the intermediate could not be isolated and styrene was the only product.

The positions assumed by the elements of methoxy mercuric acetate upon addition to a double bond are known with certainty in *dl* methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate. The *meso* form derived from methyl *cis* cinnamate was shown to have a similar structure by conversion with sodium thiosulfate to β-methoxy-β-phenylpropionic acid. Since this method failed with every other mercurial, the structures of the styrene and propenylbenzene mercurials were ascertained by bromination and subsequent elimination of hydrogen bromide with sodium methylate. The resulting α,β-unsaturated ethers were hydrolyzed to acetophenone and propiophenone. As a reliable structure proof, such a method is obviously dependent on the mechanism of bromination of these dissociable mercurials.

Bromination of these acetoxymercurials was found to proceed stepwise. The first equivalent of bromine formed the bromomercuri compound (apparently with liberation of peracetyl bromide), while the second equivalent severed the C–Hg bond to form the bromo derivative. In like manner, bromocyanogen, although incapable of breaking the C–Hg link, does react to give the bromomercurial. As another case in point, the first equivalent of acetyl chloride reacts with methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate to form the chloromercuri compound; an excess of this reagent produces methyl *trans* cinnamate.

The mercuration of 1-phenylbutadiene-1,3 proceeds stepwise and, on the basis of insecure ozonization data, the first addend enters the 3,4-positions. All attempts to establish the positions of the methoxy and mercuri groups proved fruitless. Only one of these attempts is worthy of mention. When the 3,4-[methoxychloromercuri]-1-phenylbutene-1 was reduced with one equivalent of hydrogen, using the Adams catalyst, the products were 1-phenylbutadiene-1,3 and 1-phenylbutane; the reduction proceeded as if the addend were not present.

The 1-chloromercuri-2-methoxycyclohexane initially produced from cyclohexene has been designated as the labile form, inasmuch as long refluxing in ethanol converts it to a lower melting isomer, the stable form.

The author takes this opportunity to thank Professor E. P. Kohler for the suggestions offered during the course of this work. He is also indebted to Dr. P. D. Bartlett for aid in interpreting the kinetic data.

Experimental

Titration with Potassium Thiocyanate.—When 0.001 mole of *trans* methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate was dissolved in 5 cc. of methanol and this solution thrown into 100 cc. of water, titration with standard alkali, using phenolphthalein as the indicator, showed an equivalence of one. The addition of ferric nitrate dispersed the pink color; subsequent titration with standard potassium thiocyanate showed a mercury equivalence of 0.525. This indicated a dissociation[13] of 5% since the organomercurial consumes only half of the thiocyanate required for a mercuric salt. The percentage of dissociation was unaffected by addition of 0.0005 mole of acetic acid.

A similar titration with α-acetoxymercuri-β-methoxy-β-phenylethane consumed one equivalent of alkali and one mercury equivalent of thiocyanate. Since it was evident that the thiocyanate was decomposing this mercurial, the water solution, prior to titration, was extracted twice with 5-cc. portions of chloroform (per 0.001 mole of mercurial). The water solution now contained only inorganic mercury since salts of mercury are almost insoluble in chloroform, although the organomercurials are extremely soluble in this extractant. Titration of this solution with thiocyanate showed that 0.072 equivalent of mercuric salt remained after extraction; the styrene mercurial was 7.2% dissociated.

Trans methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate was again titrated using the chloroform extraction method and the compound was found to be 2.5% dissociated. This latter figure is probably more accurate than the 5% value because the endpoint is very ephemeral when much of the organomercurial is present.

Using this method of following the mercury concentration, solutions of 0.01 mole of mercuric acetate and 0.01 mole of the unsaturated compound in methanol were made up to the desired volume and the reaction was maintained at 25 ± 2°. Samples were withdrawn at intervals, diluted with 100 cc. of water, and titrated within three minutes. Since the mercuration in water is much slower than in methanol, this error is of no significance. The rate of reaction with styrene was much too fast to be measured but at its completion 8% of the mercuric acetate remained. This checks closely with the value (7.2%) obtained for the dissociation of the mercurial in pure methanol. The reac-

---

[13] Dissociation in this sense means reversion to methoxymercuric acetate and the unsaturated compound.

tion with cyclohexene was somewhat slower but the titration (even with the chloroform extracted solution) was very erratic and at best it indicated that the acceleration due to added sodium methylate was approximately that observed in the actual preparation of the mercurial.

A series of such determinations with *cis* methyl cinnamate at concentration of 0.4, 0.2 and 0.1 molar gave a second order constant varying from 0.041 to 0.032 within the first half-life of the reaction. The second order constant for the reaction with isostilbene varied from 0.011 to 0.006, while that for *trans* methyl cinnamate was about 0.012. When the mercuration of this latter compound (at 0.2 molar) was three-fourths completed (twenty-nine hundred minutes), upon addition of 0.05 mole of sodium methylate, further titration showed the equilibrium was attained in ten minutes. The effect of prior addition of 0.05 g. of concentrated nitric acid to the 0.2 molar mercuric acetate solutions used in the *trans* methyl cinnamate and isostilbene reactions is shown in Fig. 1.

Mercuration of *trans* Methyl Cinnamate.[9]—To a solution of 3.18 g. (0.01 mole) of mercuric acetate in 25 cc. of methanol was added 0.05 g. of concentrated nitric acid, followed by 1.94 g. (0.012 mole) of methyl cinnamate. After seventy-five minutes at 25° a test portion gave no precipitate with 10% sodium hydroxide and the product began to crystallize in the reaction mixture. In a similar run, but using no nitric acid, about thirty-six hours must elapse before these conditions prevail, although the reaction is complete in eight hours when carried out at 50°. The acetoxymercuri compound was immediately filtered off (wt. 1.11 g., m. p. 142°) and the filtrate treated with dilute sodium chloride solution to yield 2.70 g. of methyl α-chloromercuri-β-methoxy-β-phenylpropionate, m. p. 134°. The total yield is 88% as compared with 84% in the analogous run using no nitric acid.

When the acetoxymercuri compound is treated with one equivalent of acetyl chloride in chloroform or acetone, the chloromercuri compound results. An excess of acetyl chloride regenerates *trans* methyl cinnamate. The chloromercuri compound is recovered unchanged from twelve hours of refluxing in ethyl acetate.

Mercuration of *cis* Methyl Cinnamate.—A solution of 1.78 g. (0.011 mole) of *cis*-methyl cinnamate[14] (m. p. −3°) and 3.18 g. (0.01 mole) of mercuric acetate in 25 cc. of methanol was filtered after nine hours and the filtrate treated with 2% sodium chloride solution. The precipitated methyl α-chloromercuri-β-methoxy-β-phenylpropionate was crystallized from ethanol to melt at 141° and weighed 2.07 g. (50%). A mixed melting point with the diastereomer obtained from *trans* methyl cinnamate (m. p. 134°) was lowered 20°.

Anal. Calcd. for $C_{11}H_{13}O_3HgCl$: C, 30.77; H, 3.05. Found: C, 31.10; H, 3.13.

When either of the diastereomers was decomposed thermally under 25 mm. pressure the distillate (*ca.* 50% of theoretical) was entirely *trans* methyl cinnamate. Under these conditions the *cis* mercurial decomposed at 157°; the *trans* decomposed at 170°. When the *cis* mercurial is refluxed for eight hours in ethyl acetate there is no tendency toward isomerization; the mercurial is recovered unchanged.

β-Methoxy-β-phenylpropionic Acid.—To a 10% sodium thiosulfate solution was added 4.52 g. (0.01 mole) of *trans* methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate. After ten minutes of agitation ether was added and the reaction set aside for twelve hours. The ether layer was separated. The aqueous layer was filtered to remove a black precipitate and the filtrate carefully acidified with 10% hydrochloric acid. The acid which slowly separated melted at 102°. It was combined with the acid of similar melting point obtained by saponification of the separated ether layer with 10% sodium hydroxide solution. Total yield was 1.09 g. or 60.5%. A similar treatment of the *cis* mercurial yields the identical acid, as does the reaction between sodium thiosulfate and anhydro α-hydroxymercuri-β-methoxy-β-phenylpropionic acid.

α-Chloromercuri-β-methoxy-α,β-diphenylethane.—After three days at room temperature a solution of 12.72 g. (0.04 mole) of mercuric acetate and 6.3 g. of isostilbene (b. p. 102° (2 mm.)) in 100 cc. of methanol was stirred while 2% aqueous sodium chloride was added slowly. The solid was filtered off and crystallized from ethanol to melt at 141°. It weighed 11.18 g. or 64% yield. Recrystallization from ethanol raised this melting point to 143°. When the reaction was refluxed the time was decreased to one-third. Addition of 0.05 g. of *concd.* nitric acid decreased the reaction time to four hours at room temperature. *Trans* stilbene could not be mercurated under any of these conditions.

Anal. Calcd. for $C_{15}H_{15}OHgCl$: C, 40.27; H, 3.38. Found: C, 40.35; H, 3.55.

Every attempt to regenerate pure isostilbene or to form α,β-diphenylethyl methyl ether failed. Treatment of the mercurial with hydrogen sulfide in alcoholic ammonia or alcoholic pyridine reaction with sodium thiosulfate, steam distillation from aqueous hydrochloric acid, oxalic acid or potassium iodide all yielded an equilibrium mixture of the isomeric stilbenes.

α-Acetoxymercuri-β-methoxy-β-phenylethane.—To a suspension of 159 g. (0.5 mole) of mercuric acetate in 1 liter of methanol was added 52 g. (0.5 mole) of styrene. The mercuric salt dissolved immediately; a test portion gave no mercuric oxide with 10% aqueous sodium hydroxide. A solution of 20 g. (0.5 mole) of sodium hydroxide in 25 cc. of water was added; following this treatment 800 cc. of methanol was distilled off. The residue was filtered and the filtrate evaporated *in vacuo*. The residue was extracted with 50 cc. of boiling benzene to remove sodium acetate and the resulting solution diluted with 1600 cc. of boiling petroleum ether (b. p. 60–70°). After a slow crystallization 117 g. (60%) of product melting at 64–65° was filtered off. The evaporated filtrate yielded 12 g. of impure product. Recrystallization from the mixed solvent raised the melting point to 70°.

Anal. Calcd. for $C_{11}H_{14}O_3Hg$: C, 33.42; H, 3.57. Found: C, 33.65; H, 3.78.

The mercurial was unchanged by twelve hours reflux with *t*-amyl alcohol. It reverted to styrene in boiling acetic anhydride but this reagent is without effect at 25°. Acetyl chloride (in acetone or chloroform), methylmagne-

---

[14] I am indebted to Professor G. B. Kistiakowsky for generously supplying the *cis* methyl cinnamate and the isostilbene used in this investigation.

sium bromide[15] or sodium thiosulfate solution (in part) only served to regenerate styrene.

α - Benzoxymercuri - β - methoxy - β - phenylethane.—A solution of 3.18 g. (0.01 mole) of mercuric acetate in 25 cc. of methanol was treated with 1.09 g. (0.011 mole) of styrene. Eight cc. of 10% aqueous sodium hydroxide (0.02 mole) was added, followed by 1.22 g. (0.01 mole) of benzoic acid. After filtration the solution was diluted with water. The crystalline precipitate weighed 3.73 g. (82%) and melted at 79°. It was crystallized from 110 cc. of petroleum ether (b. p. 60–70°) to melt at 80°. The compound was unchanged by eight hours of refluxing in toluene.

Anal. Calcd. for $C_{16}H_{16}O_3Hg$: C, 42.01; H, 3.53. Found: C, 41.73; H, 3.53.

α - Bromomercuri - β - methoxy - β - phenylethane was obtained almost quantitatively by treating the acetoxymercuri compound either with an excess of aqueous potassium bromide or with one equivalent of bromine in methanol solution at 0°. It was likewise obtained in 50% yield by treating a solution of the acetoxymercuri compound in either methanol or chloroform with two equivalents of bromocyanogen. It was crystallized from ethanol to melt at 63°.

Anal. Calcd. for $C_9H_{11}OHgBr$: C, 26.03; H, 2.67. Found: C, 26.10; H, 2.67.

Intermediate in Styrene Mercuration.—The existence of the intermediate in this reaction was demonstrated by adding 3.18 g. (0.01 mole) of mercuric acetate to a solution of 1.09 g. (0.011 mole) of styrene in 10 cc. of dioxane. After several days of intermittent shaking the reaction was filtered and the filtrate evaporated under 2 mm. pressure on a water-bath at 30°. The gummy residue was washed four times with 25-cc. portions of petroleum ether (b. p. 20–40°) and was then covered with 10 cc. of methanol. After twenty-four hours the methanol was removed *in vacuo* and the residue treated with dilute aqueous potassium bromide. The precipitate was crystallized from ethanol to give a 26% yield of the bromomercurial, melting point 63°, identified by mixed melting point.

β-Methoxy-β-phenylethyl Bromide.—Following the prescribed procedure,[4,16] a 70% yield of this compound, b. p. 84–86° (3 mm.), was obtained from the bromomercurial. The reaction is slower in chloroform solution; the mercuric bromide precipitates and the resulting solution must be washed with sodium sulfite to remove hypobromite, but the product is identical.

α-Methoxy-α-phenylethylene was obtained in 45% yield (b. p. 86–89° (18 mm.)) by refluxing this bromo compound with an excess of sodium methylate solution. It was identified by hydrolysis with 2.5% aqueous sulfuric acid to acetophenone, authenticated by mixed melting point.

β - Chloromercuri - α - methoxy - α - phenylpropane.—A solution of 15.9 g. (0.05 mole) of mercuric acetate in 125 cc. of methanol was treated with 6.89 g. (0.058 mole) of phenylpropene-2 (b. p. 57.5–58° (10 mm.)). Within four hours a test portion gave no mercuric oxide with 10% aqueous sodium hydroxide. At the end of eighteen hours 0.05 mole of sodium methylate solution was added. Twenty-four hours later the reaction was filtered and the solvent removed *in vacuo*. The residue was shaken with 2% aqueous sodium chloride. After an hour the aqueous layer was decanted and the gummy residue extracted with 100 cc. of boiling ethanol. Six days elapsed before crystal clusters formed which were filtered off and crystallized from ethanol to melt at 95–95.5°, weight 4 g. or 21%.

Anal. Calcd. for $C_{10}H_{13}OHgCl$: C, 31.17; H, 3.40. Found: C, 31.00; H, 3.40.

Since the mother liquors were not amenable to further crystallization the solvent was removed *in vacuo* and the residue was dissolved in 50 cc. of chloroform followed by 4.8 g. (0.03 mole) of bromine. After twenty-four hours the colorless solution was decanted from mercuric salt and washed with iced sodium sulfite solution, then with water and finally dried with anhydrous sodium sulfate. Following evaporation of the solvent the residue was distilled under 14 mm. pressure. The distillate, b. p. 107–125°, wt. 2.24 g., was refluxed for five hours with 0.05 mole of sodium methylate solution. The methanol was removed by evaporation, the residual oil being taken up in ether, washed to neutrality with water, dried with anhydrous sodium sulfate and distilled *in toto*. The distillate was hydrolyzed with alcoholic hydrochloric acid[17] and the semicarbazone prepared directly from this solution. This derivative contained an alkali insoluble impurity which was crystallized from methanol to melt at 183°. However, the great part of the product was precipitated by neutralizing the alkaline solution and was crystallized from ethanol to melt at 173–174°. A mixed melting point with propiophenone semicarbazone was not lowered.

β-Bromo-α-methoxy-α-phenylpropane was prepared from 0.01 mole of the pure β-chloromercuri-α-methoxy-α-phenylpropane and 0.02 mole of bromine in chloroform solution essentially as described above. The product boiling at 122–125° weighed 1.35 g. (92%), $n^{26}\text{D}$ 1.5412.

α-Methoxy-α-phenylpropene was prepared from this bromo compound, by the procedure already described, in 31% yield as an oil, b. p. 96–97° (19 mm.), $n^{26}\text{D}$ 1.5347. It was identified by hydrolysis with alcoholic hydrochloric acid; the semicarbazone prepared from this solution showed no depression in melting point when mixed with propiophenone semicarbazone.

Labile 1-Chloromercuri-2-methoxycyclohexane.—A solution of 9.84 g. (0.12 mole) of cyclohexene in 250 cc. of methanol was treated with 3.8 g. (0.1 mole) of mercuric acetate. A test portion removed immediately upon solution of the mercuric salt gave no mercuric oxide with 10% aqueous sodium hydroxide. After thirty-six hours the mercurous salt was filtered off and the filtrate evaporated *in vacuo*. Alternatively if, after a reaction period of ninety minutes, 0.1 mole of sodium methylate solution is added, the reaction can be worked up shortly afterward and the solvent can be removed at atmospheric pressure. The residue was suspended in water and 10% aqueous sodium chloride was added. When the precipitated oil solidified after occasional agitation, it was filtered off. This crude product, wt. 33 g., m. p. 109°, was crystallized from ethanol to weigh 26 g. (75%) and melted at 114–115°. Further purification from a solution of 150 cc. of benzene and 30 cc.

---

(15) Middleton, This Journal, **45**, 2763 (1923).

(16) Kohler, *ibid.*, **52**, 3728 (1930).

(17) Lauer and Spielman, *ibid.*, **53**, 1533 (1931).

of petroleum ether (b. p. 30–60°) did not raise the melting point.

Anal. Calcd. for $C_7H_{13}OHgCl$: C, 24.07; H, 3.75. Found: C, 23.97; H, 3.92.

Stable 1 - Chloromercuri - 2 - methoxycyclohexane.—When the labile mercurial is refluxed for fifteen hours in ethanol, an isomer, m. p. 86°, crystallizes almost quantitatively from the filtered solution. The melting point is not raised by further crystallization from ethanol.

Anal. Calcd. for $C_{17}H_{13}OHgCl$: C, 24.07; H, 3.75. Found: C, 24.06; H, 3.79.

Intermediates in Cyclohexene Mercuration.—To a solution of 2.7 g. (0.01 mole) of mercuric chloride in methanol was added a solution of 0.23 g. of sodium in 10 cc. of methanol. To the suspension of white precipitate was added 0.98 g. (0.012 mole) of cyclohexene. After twenty-four hours the white precipitate was filtered off; it contained no cyclohexene mercurial and rapidly became yellow in presence of moisture. The filtrate was concentrated *in vacuo* and the residue treated with dilute aqueous sodium chloride. The precipitate was crystallized from ethanol to weigh 0.15 g. (4%). It was 1-chloromercuri-2-methoxycyclohexane, m. p. 114–115°, identified by mixed melting point.

When 0.02 mole of sodium methylate was used under otherwise identical conditions the yield of mercurial was 5%.

Demonstration of the type of intermediate encountered with styrene (*vide supra*) could not be reproduced when 0.01 mole of mercuric acetate was dissolved (with comparative ease) in 5 cc. of cyclohexene. After twenty-four hours the excess of cyclohexene was removed at 30° under 25 mm. pressure and the oily residue extracted five times with 25-cc. portions of petroleum ether (b. p. 20–40°) The washed residue was treated with dilute sodium chloride solution. No chloromercurial could be isolated from the precipitate.

1-Lactomercuri-2-methoxycyclohexene.—Mercuric lactate was prepared by treating a solution of 31.8 g. (0.3 mole) of 85% lactic acid in 200 cc. of water with 21.6 g. (0.1 mole) of red mercuric oxide. After two days with occasional shaking the solution was filtered and the solvent removed *in vacuo*. The residue was diluted with 100 cc. of ethanol. Next day the granular solid was filtered off and washed with alcohol; it weighed 17 g., after drying over sulfuric acid, and melted at 144° with decomposition. Evaporation of the alcoholic filtrate in a current of air yielded successive fractions of impure salt.

To a suspension of 3.78 g. (0.01 mole) of this salt in 25 cc. of methanol was added 0.98 g. (0.012 mole) of cyclohexene. After two days 4 cc. of 10% aqueous sodium hydroxide was added, the solution filtered and the solvent removed *in vacuo*. The residue was extracted with 80 cc. of boiling petroleum ether (b. p. 90–120°). The compound crystallizing therefrom weighed 1.74 g. (43%) and melted at 91–92°. It was recrystallized from the same solvent for analysis (m. p. 92°).

Anal. Calcd. for $C_{10}H_{18}O_4Hg$: C, 29.81; H, 4.51. Found: C, 29.44; H, 4.61.

Chloromercurimethoxyphenylbutene.—To a solution of 3.18 g. (0.01 mole) of mercuric acetate in 25 cc. of methanol was added 1.56 g. (0.012 mole) of freshly distilled phenyl butadiene. After five minutes a test portion gave no precipitate of mercuric oxide with 10% aqueous sodium hydroxide. After four hours the reaction was filtered to remove mercurous salt and 10% aqueous sodium chloride was added slowly to the filtrate. The oil which precipitated soon solidified and was filtered, washed twice with water and twice with petroleum ether. The yield of product melting at 89° was 3.35 g. (85%). It was crystallized from 25 cc. of ethanol to melt at 92°.

Anal. Calcd. for $C_{11}H_{13}OHgCl$: C, 33.25; H, 3.30. Found: C, 33.52; H, 3.37.

Following an identical procedure bromomercurimethoxyphenylbutene was obtained by substituting a solution of potassium bromide. The yield was 4 g. (91%) melting at 75–76°. This was crystallized from 35 cc. of ethanol to melt at 76°.

Anal. Calcd. for $C_{11}H_{13}OHgBr$: C, 29.90; H, 2.97 Found: C, 29.57; H, 2.97.

Ozonization of Chloromercurimethoxyphenylbutene.—A solution of 3.97 g. (0.01 mole) of the mercurial was dissolved in 12 cc. of dry chloroform. This solution was ozonized at 0° for five hours. The solvent was removed in a stream of dry, oxygen-free nitrogen. After adding 10 cc. of water the nitrogen stream was continued for two days; the outlet tube bubbled through a solution of phenylhydrazine hydrochloride. The benzaldehyde phenylhydrazone thus formed (70%) melted at 148–150° and after purification was identified by mixed melting point. A test portion taken from the aqueous suspension of decomposed ozonide at this time gave no mercuric oxide with 10% sodium hydroxide. The aqueous layer was decanted off and the residue washed thoroughly with ether. This residue was then covered with 10 cc. of 5:8 aqueous hydrochloric acid and the passage of nitrogen was resumed but no odor of acrolein could be detected, nor was phenylpyrazoline found in the absorption tube. After twenty-four hours the acid layer when treated with sodium hydroxide precipitated mercuric oxide. The remainder of the decomposed ozonide was found to be chiefly mercurous chloride.

Diacetoxymercuridimethoxyphenylbutane.—To a solution of 6.36 g. (0.02 mole) of mercuric acetate in 55 cc. of methanol was added 1.43 g. (0.011 mole) of phenylbutadiene (b. p. 86° (11 mm.)). After two hours a test portion gave no precipitate with 10% aqueous sodium hydroxide. Twelve hours later 40 cc. of methanol was distilled off and the residue filtered and chilled to 10°. The crystalline product weighed 7.62 g. (35%) and melted at 142–145°. Crystallization from a mixture of 25 cc. of benzene and 35 cc. of petroleum ether (b. p. 60–70°) raised the melting point to 149° with little loss of material.

Anal. Calcd. for $C_{16}H_{22}O_6Hg_2$: C, 27.00; H, 3.12; Hg, 56.40. Found: C, 26.53; H, 3.18; Hg, 56.43.

This procedure was varied by using a 33% excess of mercuric acetate and, subsequent to the twelve-hour reaction period, adding sodium methylate solution until appearance of the first permanent yellow coloration. The reaction after a day was worked up as before to give a 60% yield based on the phenylbutadiene.

Dichloromercuridimethoxyphenylbutane.—A solution of 0.4 g. (0.001 mole) of chloromercurimethoxyphenylbutene in 5 cc. of methanol was treated with 0.32 g. (0.001 mole) of mercuric acetate. The latter dissolved immediately but test portions gave a precipitate with 10% aqueous sodium hydroxide for twelve hours. After thirty-six hours a solution of 10% sodium chloride was added. The precipitated solid melted roughly at 100°. After washing with hot ethanol it melted at 180° and weighed 0.16 g. The compound can be obtained more easily by treating the diacetoxymercuridimethoxyphenylbutane in methanol with exactly two equivalents of dilute hydrochloric acid. The compound crystallizes slowly from acetone.

Anal. Calcd. for $C_{12}H_{16}O_2Hg_2Cl_2$: C, 21.68; H, 2.43. Found: C, 21.60; H, 2.52.

Summary

1. The rate of mercuration of ethylenes has been found to depend on a bimolecular reaction.
2. Some *cis* ethylenes mercurate more rapidly than the *trans* isomers.
3. An alternative mechanism is suggested to explain the mercuration.

CAMBRIDGE, MASS. RECEIVED APRIL 5, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VASSAR COLLEGE]

The Reaction between 2,3-Dimethyl-1,4-naphthoquinone and Phenylmagnesium Bromide.[1] I

BY H. MARJORIE CRAWFORD

Numerous studies have been made of the reactions between quinones and Grignard reagents. Only in the cases of anthraquinone[2] and phenanthraquinone[3] were the reactions clean-cut and the yields good. The mono- or di-addition product resulted, depending on the relative amounts of reactants.

If there was a possibility of a 1,4 addition to a conjugated system besides the addition to the carbonyl group, the reactions were complicated, many different products resulted and tars and oils formed the main products of the reaction. Bamberger[4] studied the reaction of methylmagnesium iodide on *p*-xyloquinone and identified six solid products which accounted for only one-fourth of the quinone used. Another fourth was reduced to the hydroquinone, and amorphous solids and oils remained. Franssen,[5] using α-naphthoquinone, isolated a di-addition product in 25% yields, but obtained colored amorphous products, reduction products and tars. Thinking that these complex results might have been due to hydrogen atoms attached to the quinone nucleus, Smith and Crawford[6] studied the reaction between a fully substituted quinone (duroquinone) and phenylmagnesium bromide and found that in this case also the reaction was very complex. The main product of the reaction was an oil (80%) and from the other 20% eight solids were separated and identified. 1,2- and 1,4-addition occurred as well as reduction and the formation of double compounds of the quinhydrone type.

Discussion of the Reaction and Products

In the present work, 2,3-dimethyl-1,4-naphthoquinone was chosen because it appeared to be intermediate in structure between duroquinone, which gave complex results, and anthraquinone which gave clean-cut results. However, it seems that as long as any 1,4-conjugated system is open the reaction is complicated, even though one side of the quinone is blocked by a benzene ring. The predicted mono- and di-addition products were obtained as well as double compounds, reduction products and dehydration products.

Three types of reaction products were formed and will be discussed separately, although all were formed at the same time. If one or one and a half moles of phenylmagnesium bromide was used per mole of the quinone, mono- and di-addition products were formed. If two moles of phenylmagnesium bromide were used per mole of quinone, di-addition products predominated.

A. Reduction Products.—The reduction of quinones by Grignard reagents is quite general and, regardless of procedure, reduction products

---

[1] Presented in part at the New York meeting of the American Chemical Society in April, 1935.

[2] (a) Haller and Guyot, *Compt. rend.*, **138**, 327 and 1251 (1904); (b) Guyot and Staehling, *Bull. soc. chim.*, **33**, 1104 and 1144 (1905); (c) Haller and Comtesse, *Compt. rend.*, **150**, 1290 (1910); (d) Clarke and Carleton, THIS JOURNAL, **33**, 1966 (1911).

[3] (a) Werner and Grob, *Ber.*, **37**, 2887 (1904); (b) Zincke and Tropp, *Ann.*, **362**, 242 (1908); (c) Bachmann and Chu, THIS JOURNAL, **57**, 1095 (1935).

[4] Bamberger, *Ann.*, **384**, 272 (1911).

[5] Franssen, *Bull. soc. chim.*, **37**, 902 (1925); **45**, 1030 (1929).

[6] Smith and Crawford, THIS JOURNAL, **50**, 869 (1928).