The Hydrocarbons, 1,2-Tetral-9,10-diphenylanthracene XII.—When the diol X (1 g.) was heated at 150° for an hour and a half it gave a resin from which was isolated 0.4 g. of the hydrocarbon. The latter is obtained analytically pure only after passing over alumina in a Tswett column. It separates from dioxane or chloroform in yellow prisms (m. p. 295°) that show a bluish-violet fluorescence; the latter is not nearly as bright or as blue as that of the isomeric linear hydrocarbon.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.7; H, 6.3. Found: C, 93.4; H, 6.2.

The hydrocarbon also was obtained in a yield of 70% by reduction of the diol by potassium iodide in acetic acid.

9,10-Diphenylanthracene.—The highest yield of diol obtained from anthraquinone by the above standardized procedure was 88%. The yield was 86% when the reaction was carried on at the boiling point of butyl ether, 141°.

The bluish fluorescence typical of diphenylanthracene appeared whenever a solution of the diol in any solvent was heated above about 100°. Although this fluorescence was noticed when the diol was treated with magnesium and magnesium bromide, there was insufficient hydrocarbon formed to isolate. However, during the working up of the residues with acetic acid (one hour), a 1% yield of the hydrocarbon was secured; when an acetic acid solution was refluxed for forty-eight hours, the diphenylanthracene was isolated in a yield of 40%. One would thus conclude that acetic acid favors the formation of the hydrocarbon.

Summary

A study of the action of phenylmagnesium bromide upon a variety of anthraquinones under standardized conditions has been made. Simple and angular benz-anthraquinones gave diols.

Linear benz-anthraquinones gave diols (1,2-addition) and ketones (1,4-addition) in the absence of magnesium. In the presence of this metal, the hydrocarbon corresponding to the expected diol resulted. It has been shown that the hydrocarbon formation is due to the combination of magnesium–magnesium bromide.

A possible relationship between the types of reaction and bond structures has been pointed out.

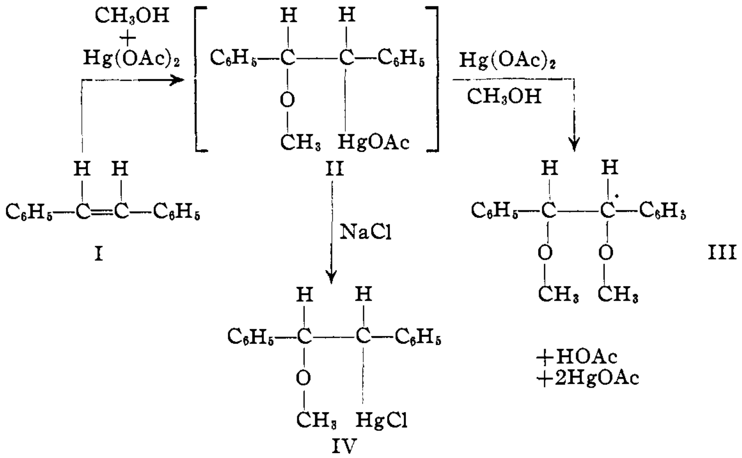
ROCHESTER, NEW YORK RECEIVED JUNE 17, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

Catalysis in the Formation of α-Methoxymercurials from Ethylenes

BY A. M. BIRKS AND GEORGE F. WRIGHT

It has been reported[1] that *trans*-stilbene, in contrast to *cis*-stilbene, does not react with mercuric acetate in methanol solution to form, after treatment with sodium chloride, 1-chloromercuri-2-methoxy-1,2-diphenylethane, IV. This reaction was recently re-investigated in this Laboratory because it had been observed that, although no mercurial could be isolated, a considerable amount of mercurous salt was precipitated from the reaction solution over a period of days. It was, indeed, found that all of the equivalent quantity of mercuric acetate was reduced in fifteen days at 25°. If this solution were then heated with a second equivalent of mercuric acetate for four days, 1,2-dimethoxy-1,2-diphenylethane could be isolated in 20% yield. The 1-chloromercuri-2-methoxy-1,2-diphenylethane from *cis*-stilbene, when heated in methanol solution with mercuric acetate, likewise gave this compound. It therefore seemed probable that *trans*-stilbene did react to form a mercurial, II, but so slowly that it was converted by unconsumed mercuric acetate to the dimethoxy compound, III.



Although nitric acid had been used as an accelerator for preparation of other methoxymercurials,[1,2] it seemed to have no effect on the reaction with *trans*-stilbene. We guessed that this catalyst exerted a peroxide

---

[1] Wright, THIS JOURNAL, **57**, 1993 (1935).

[2] Brown and Wright, *ibid.*, **62**, 1991 (1940).

effect, since nitric acid (peroxide-free in water) in methanol gave a faint test for peroxide with titanium trichloride after a few hours.[3] Instead of nitric acid, therefore, one-tenth equivalent of such typical peroxides as benzoyl peroxide or ascaridole was added to the reaction mixture. Under these conditions of greater peroxide content than could be furnished by nitric acid in methanol, *trans*-stilbene was converted in one day to a 1-chloromercuri-2-methoxy-1,2-diphenylethane in 24% yield and diastereomeric with the higher melting form obtained from *cis*-stilbene. It should be pointed out in passing that, whenever diastereomeric pairs have been isolated (α-methoxymercurials from methyl cinnamates,[1] styryl cyanides,[2] Δ^2-butenes and now stilbenes) that one obtained from the *trans* geoisomer always melts lower than the diastereomer from the *cis* form.

The addition to *trans*-stilbene was not followed kinetically because of the insolubility of this ethylene in methanol, but it was far from complete since the greater part of the stilbene was recovered unchanged. A longer reaction period resulted in a complex mixture from which no compound could be isolated, although the dimethoxydiphenylethane was probably present.

Since the accelerating effect of nitric acid was thus related to its peroxide-forming ability in methanol, a general study of the catalysis was undertaken. Two substances were chosen as representative ethylenes: benzalacetophenone, which reacts without catalyst,[4] and the styryl cyanides,[2] which require catalyst before any reasonable amount of reaction can be detected. Both substances were found by titanium trichloride and ferrous sulfate–thiocyanate tests to be peroxide-free.

Although peroxides initiated reaction between styryl cyanide and mercuric acetate in methanol, the catalysts were destroyed so quickly that the reaction could not be carried to completion. This indicates that nitric acid is the preferred catalyst in systems which consume peroxide since it provides a small but constant source of the accelerator during the entire reaction period.

Peroxide-free benzalacetophenone reacts rapidly at 35° with mercuric acetate in methanol, the rate being affected by the quality of the mercuric acetate used. Thus the plot of reciprocal concentration against time (Fig. 1) showed that mercuric acetate obtained from the British Drug House, Ltd., reacted most slowly (E) while that obtained from Mallinckrodt was somewhat better (C). Crystallization of the latter accelerated the rate (B) and this purified reagent was used throughout the work unless otherwise specified. We were unable to find the impurity which caused these variations. Addition of peroxide had little effect; thus, 0.2 equivalent of dimethyl peroxide added to the purified mercuric acetate caused a slight acceleration (A), but addition of 0.45 equivalent of peracetic acid to the British Drug House reagent caused a very slight retardation (F). The course of the reaction is seen from these curves to be second order in every case. The reaction using purified mercuric acetate without catalyst (B) maintained this second order rate over three-fourths of the life, this time being shown by a cross-bar on the curve. About this time mercurous salt began to separate. The same product, α-acetoxymercuri-β-methoxy-β-phenylpropiophenone, V, was obtained, whether or not peroxide was present.

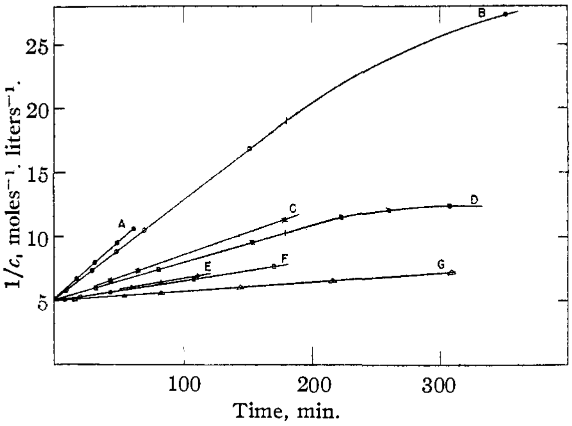


Fig. 1.

There was thus a marked contrast between styryl cyanide, which adds the methoxymercuric acetate elements very slowly except when peroxide is present, and benzalacetophenone, which undergoes this reaction readily and almost independently of peroxide. It occurred to us that since the styryl cyanides were much less reactive toward this addition reaction than were a number of closely related substances,[1] the cyano group was probably responsible. Accordingly acetonitrile was added to the benzalacetophenone–mercuric acetate solution in methanol. It was found that one equivalent of this substance retarded the rate from a half-life of sixty minutes

---

(3) Mr. J. C. Bond had ascertained previously that lithium nitrate exerted no catalytic effect on the addition reaction.

(4) Middleton, THIS JOURNAL, **45**, 2763 (1923).

for the uninhibited reaction (Fig. 2E) to one hundred and eighty minutes (Fig. 2C). The course of the retarded reaction was still second order (Fig. 1D) and the yields of the same product were identical. It is, perhaps, more than coincidence that the rate of the inhibited reaction falls off at half-life (cross-bar on curve) *but in approximately the same length of time* required for three-fourths life of the uninhibited reaction. In both cases mercurous salt began to appear at the time that the rates fall off.

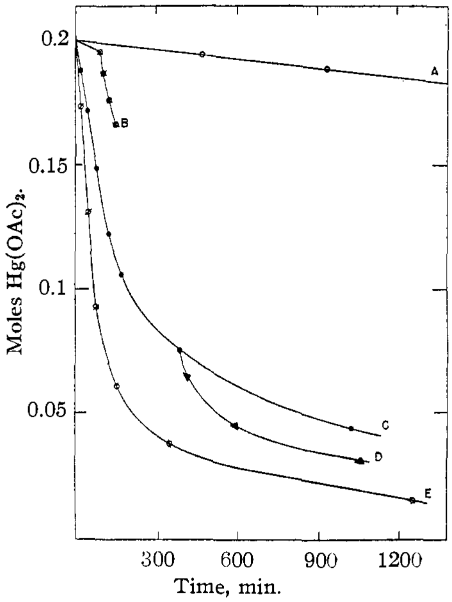


Fig. 2.

In order to relate the peroxide-acceleration observed when styryl cyanide and mercuric acetate react in methanol to the inhibiting effect of acetonitrile, the experiment with an equivalent of the latter substance was repeated with benzalacetophenone. The consumption of mercuric acetate again followed curve C, Fig. 2, until, at approximately two-thirds life, an equivalent of hydrogen peroxide was added. It may be seen (Fig. 2D) that the peroxide restores the rate practically to its original uninhibited value (compare D and E). Finally it was found that an equivalent amount of styryl cyanide added to the benzalacetophenone inhibited the reaction as did acetonitrile. The rate curve using either nitrile as inhibitor is identical. The effect must therefore be a function of the cyano-group in these substances.

The cyano-group is not, however, specific. The inhibiting effect of pyridine is even more pronounced. One equivalent of either this substance or its acetate almost stopped the reaction with benzalacetophenone (Fig. 2A, completion requires eleven days instead of twelve hours uninhibited) while 0.1 equivalent retarded it to less than one-tenth its normal rate, as is shown by the first part of curve B, Fig. 2. The increase in rate shown in curve B to a value comparable with the uninhibited rate was caused by addition of 0.1 equivalent of hydrogen peroxide. The results therefore parallel those found with the nitriles.

Since not more than a trace of peroxide could have been present in the uncatalyzed reaction mixture, the fact that one equivalent of pyridine is more effective than one-tenth equivalent indicates that the action of the retarding agent is not simply one of peroxide removal. More significantly, none of the retarding substances are efficient as antioxidants although pyridine does act slowly on hydrogen peroxide over a period of hours. Here, however, the effect is immediate. Furthermore, diethyldisulfide, which might be expected to resemble the peroxides, was found to retard the addition of the elements of methoxymercuric acetate to benzalacetophenone.

The behavior of this inhibitor gave significant information concerning retardation of the addition reaction. Although the end-point was obscure the reaction could be followed titrimetrically; the titration was initially low by 22% when 0.1 equivalent of diethyldisulfide was used. Since this indicated reaction between mercuric acetate and the disulfide, equimolar quantities of these substances were mixed in methanol. From an aliquot of this solution, carried through the customary procedure involving chloroform extraction, there could be found by thiocyanate titration only 7.6% of the mercury which should have been present. Evaporation of the methanol solution of the substance left a residue from which, by chloroform extraction, a compound could be separated from insoluble mercuric acetate. This compound, according to analysis, proved to be the mixed mercuric salt of acetic acid and ethyl mercaptan. In conformity with this structure it gave an infusible compound with sodium chloride resembling chloromercuric ethylmercaptide.[5] Both compounds yielded ethyl mercaptan upon acidification with hydrochloric acid. The acetoxymercuric ethylmercaptide evidently was present in solution in mobile equilibrium with mercuric acetate and diethyldisulfide, because the addition

---

(5) Challenger and Rawlings, *J. Chem. Soc.*, 868 (1937).

reaction to benzalacetophenone was second order when 0.1 equivalent of diethyldisulfide was used as inhibitor. This is shown by curve G, Fig. 1, the values having been obtained by correcting the titrations for the 22% error which this amount of diethyldisulfide had been shown to introduce. It may be significant that of the three substances which exert a retarding effect, acetonitrile and pyridine are commonly known to form coördination complexes with great ease, and a salt is formed between mercuric acetate and diethyldisulfide in methanol.

A consideration of the catalysts used thus far showed that the peroxides were electron acceptors in contrast to pyridine and the nitriles, which were electron donors, the case of diethyldisulfide being in this sense anomalous. On this basis it might be predicted that boron salts, being acceptors should accelerate the addition reaction. A boron acetate was prepared but was found to have no appreciable effect on the reaction with *cis*-styryl cyanide. Before boron trifluoride was tried, a methanol solution of the etherate was treated with both *cis*- and *trans*-styryl cyanides for two days without any detectable amount of isomerization taking place. When it had been ascertained that fluoride, in contrast to the other halides, did not interfere with the thiocyanate titration, boron trifluoride etherate was used with styryl cyanide. It was found to be an accelerator as predicted.

Although 0.1 equivalent of boron trifluoride etherate would cause a marked acceleration of the addition to *cis*- and *trans*-styryl cyanides, the reactions stopped after a few hours. They could be started again by further addition of this catalyst. The rate is shown as reciprocal concentration against time in Fig. 3 where curve C represents the catalysis at 35° of 0.2 molar *trans*-styryl cyanide and mercuric acetate in methanol with 0.1 equivalent of the trifluoride; the cross-bar indicates one-seventh life. Curves A and B denote use of one and 0.86 equivalents of catalyst, respectively, in otherwise identical experiments, the cross-bars representing half-life. In each case the rate dropped off sharply after twenty minutes and the reactions practically stopped after forty minutes, but were reasonably second order in the early stages when the larger amounts of catalyst were used. The extension of curve A, using 1 equivalent of catalyst, showed that the reaction stopped when the consumption of mercuric acetate was about three-fourths complete. No chloromercurial could be isolated from the experiment represented by curve C, and only a few per cent. from those represented by A and B. In contrast, the half-life of the reaction with *cis*-styryl cyanide was four minutes when one equivalent of boron trifluoride was added, the reaction was complete in two hours, and a good yield of chloromercurial was obtained.

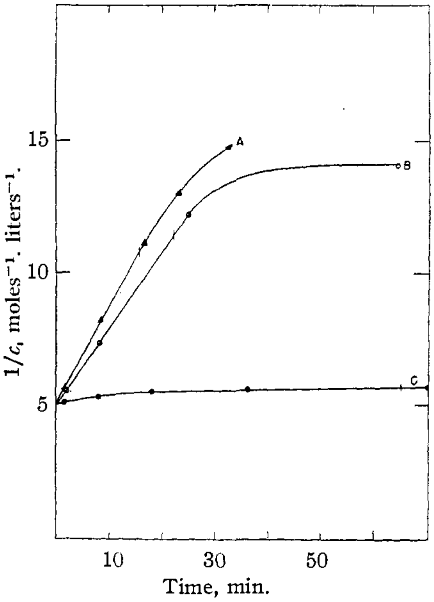


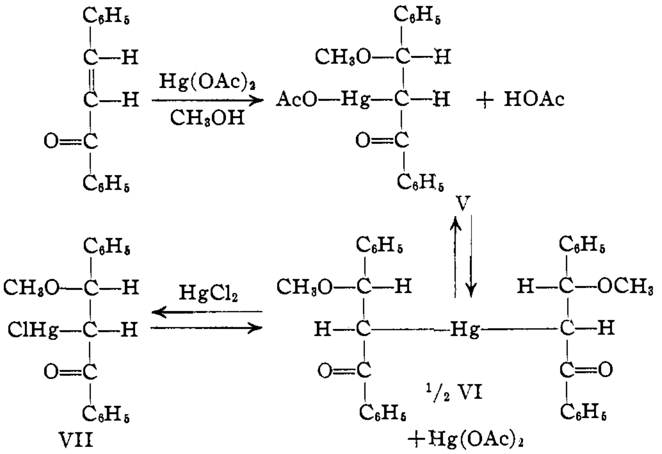
Fig. 3.

The contrast in yields of mercurial from the *cis* and *trans* geoisomers was partly explained by a study of the products. Because of the fluorine-containing catalyst which was present it was considered necessary to isolate the chloromercurials rather than the acetoxymercurials. In order to correlate these new derivatives with the acetoxymercuri compounds already known,[2] the latter were converted by the customary method with sodium chloride. The diastereomer from the *cis*-nitrile was easily formed in a state of purity, but an indefinite mixture of wide melting range was obtained from the diastereomer formed from *trans*-styryl cyanide, and this mixture decomposed upon attempted crystallization. It was somewhat surprising to find that this was evidently a mixture of RHgCl and R_2Hg. The instability of the mixture was probably caused by presence of the latter type which has not been known heretofore among the α-methoxymercurials. It was likewise unexpected because, although organomercuric iodides are prone to dismutate into the

R_2Hg type, there is usually no tendency for RHgBr and RHgCl to do likewise. Actually the R_2Hg compound was not isolated, but its presence was substantiated by the fact that when the mixture was treated with an excess of mercuric chloride the equilibrium $2RHgCl \rightleftarrows R_2Hg + HgCl_2$ was forced so completely to the left that the melting point was raised 60° and within a degree of the melting point of the thoroughly purified compound which was finally obtained. The trouble encountered here suggests that in instances where other methoxymercurials have formed as non-crystallizable oils, the unsuspected equilibrium mixture was present, which could not have been purified owing to the sensitive R_2Hg present. Results might have been obtained in these instances if the oil had been forced into the RHgCl form by treatment with an excess of mercuric chloride.

Although the chloromercurial addition product of *trans*-styryl cyanide was thus brought to hand from the previously known α-acetoxymercuri-β-methoxy-β-phenylpropionitrile by forcing the equilibrium toward the RHgCl state, its isolation from the boron trifluoride-catalyzed reaction did not succeed by such treatment alone. This might have been expected from the sudden deviation from second order rate after the reaction had progressed about twenty minutes. The cessation of reaction before the mercuric salt was entirely consumed could not be explained as attainment of a measurable equilibrium between the acetoxymercurial and the starting materials, because it had previously been determined[2] that such an equilibrium does not exist in this reaction. Furthermore, none of the characteristic odor of styryl cyanide could be detected at the end of the reaction when the solution was poured into water. The product was a gum which melted at 50–90° after treatment with mercuric chloride and sodium chloride. Small amounts of the expected α-chloromercuri-β-methoxy-β-phenylpropionitrile could be isolated from this with great difficulty owing to a less soluble impurity. If, however, the separation for analysis were simulated for the entire reaction mixture, it was found that mercuric chloride–sodium chloride treatment of the chloroform extract gave the desired diastereomer in a yield of 50%. The residual aqueous solution, following chloroform extraction, precipitated an organomercurial when treated with mercuric chloride and sodium chloride. This infusible compound has not been identified. Analysis indicates that it contains much more mercury than the methoxymercurial. The detection of this chloroform insoluble acetoxymercurial by-product affords an explanation for the observed deviations from second order rate since it remains in the water layer during analysis. Since thiocyanate will be consumed by organomercurials of this type, it will be evaluated as inorganic mercury, and hence will falsely indicate that mercury consumption is too slow for a second order rate. The formation of this by-product seems to be a slower reaction than the normal addition and may be subsequent to the addition since optimum yields are obtained by rapid, catalyzed reaction and immediate processing of the reaction mixture.

While the source of error just outlined obscures positive evidence of other effects in the addition to styryl cyanide, the possibility should not be excluded that some deviation from second order rate is caused by a subsequent equilibrium of the type $2RHgOAc \rightleftarrows R_2Hg + Hg(OAc)_2$. This possibility can be realized in the case of the cleaner reaction with benzalacetophenone. The latter reaction may be accelerated so that it is complete in six minutes when 0.1 equivalent of boron trifluoride etherate is used as catalyst, a fact that is somewhat surprising in view of the insignificant effect of peroxide on this addition. Whether or not this addition is rendered fast or slow by catalyst addition, the reaction always ceases when 10–12% of the uncombined mercuric salt can still be titrated following the analytical procedure. This indicates that the following series of reactions occur



According to this formulation the mercuric acetate originating from the dismutation ought to be available for reaction with a second equivalent of benzalacetophenone to yield entirely the product R_2Hg. Addition of a second equivalent does reduce the uncombined mercury content to zero, but no success has attended the isolation of VI. This is not surprising, because those reagents which tend to convert RHgX into R_2Hg invariably yield the parent ethylene when used on methoxymercurials such as II, IV, V and VII; it is evident that the R_2HgX structure is unstable when linked vicinally with methoxyl. We have, however, demonstrated the presence of VI in the solution by introducing mercuric chloride (which will not add by this mechanism to ethylenes) into the solution after having allowed sufficient length of time so that the reaction V $\longrightarrow$ VI was complete. In this way the reaction VI $\longrightarrow$ VII was effected, the yield of 89% indicating that VI must have been present. Indeed this seems to be the most satisfactory method of effecting the addition of the elements of methoxymercuric chloride to an ethylene and undoubtedly is partly responsible for the improvement in rate constancy observed[2] when two equivalents of *cis*-styryl cyanide were treated with one equivalent of mercuric acetate in methanol. It should be noted that reaction VI $\longrightarrow$ VII is not instantaneous and should be allowed a reasonable length of time for completion. The equilibrium and its rate of attainment is being studied in this Laboratory in connection with the similar phenomenon observed with other organometallic compounds.

While it would appear from this work that boron trifluoride was the preferred catalyst for acceleration of the addition reaction, it was found unsatisfactory for use with *trans*-stilbene. Reaction occurred, to be sure, very rapidly and little mercurous salt precipitated. This was, however, evidently owing to the solubility of the mercurous fluoride in methanol, because the reaction product contained only unchanged stilbene and hydrobenzoin dimethyl ether, with no trace of the mercurial.

Discussion

Any hypothesis concerning the action of these catalysts must necessarily depend on the mechanism by which the addition of the methoxymercuric acetate elements to an ethylene takes place. This mechanism may be classified as one wherein each geometric isomer yields its characteristic diastereomer uncontaminated by the other form. In spite of careful searches for diastereomeric mixtures arising from a number of geoisomeric pairs, no such mixture has been detected. This reliability with respect to diastereomer formation prevails throughout the catalyzed reactions described in this paper.

The addition of the methoxymercuric acetate elements resembles in this respect the careful addition of the hydrogen peroxide elements to ethylenes.[6] It may be contrasted to bromine addition, which seems to give the saturated compound characteristic of a certain geoisomer only in reactions which are very rapid and probably require a low activation.[7] In slower reactions involving a higher activation energy, mixtures of isomers frequently are obtained. Both *cis*- and *trans*-stilbenes, for example, give diastereomeric mixtures with bromine.[8] Both of the styryl cyanides yield the same dibromide, evidently related to the *trans* form, by a slow reaction. Regardless of the speed of the reaction, each of these four geoisomers gives only its characteristic diastereomer when treated with mercuric acetate in methanol. This difference between bromine addition and methoxymercuric acetate addition is probably owing to the low activation required for the latter (estimated as an average of about 8000 cal.).

It is therefore improbable that the catalysts effective in methoxymercuric acetate addition act upon the ethylene by any mechanism involving either an intermediate carbonium ion or a free radical, since either would be expected to racemize and hence give rise to diastereomeric mixtures. Whereas such intermediates may provide alternative mechanisms for bromine addition if the energy requirements are less than, or approximately equal to, that necessary for non-fragmentary addition, there seems to be no alternative mechanism for addition of the methoxymercuric acetate elements other than as a single unit, whether or not a catalyst is employed.

The earlier suggestion[1] that an accelerating catalyst affected only the formation of methoxymercuric acetate is not borne out by the present investigation since it necessarily implies that specific catalysts would have a comparable ef-

---

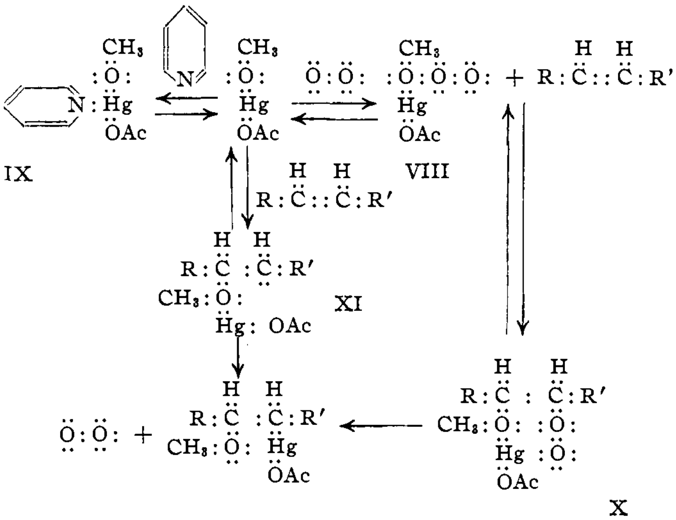
[6] Braun, THIS JOURNAL, **51**, 228 (1929).

[7] (a) Young, Dillon and Lucas, *ibid.*, **51**, 2525 (1929). (b) Young, Pressman and Coryell, *ibid.*, **61**, 1640 (1939).

[8] Wislicenus and Seeler, *Ber.*, **28**, 2693 (1895).

fect toward ethylenes in general. On the contrary it has been shown here that, although boron trifluoride powerfully catalyzes addition to either benzalacetophenone or the styryl cyanides, only the latter of these substances is significantly affected by peroxides.

The following mechanism seems more in accord with the evidence presented in this paper.



Oxygen and pyridine are illustrated as typical of the two classes of substances upon which the rate is dependent. The former, an electron acceptor, coördinates with the methoxyl oxygen to give VIII while the electron donor (pyridine) coördinates with the mercury atom to give IX. In the latter case addition is inhibited owing to the decreased activity of the complex. In VIII, on the other hand, the coördinated peroxide acts as a carrier *via* X to effect a deactivation process through regeneration of the acceptor. This does not exclude the uncatalyzed reaction proceeding through the configurationally stable carbanion XI and it further explains, on the basis of the stability of X, why certain catalysts are more effective toward one ethylene than toward another.

Experimental

Preparation of 1,2-Dimethoxy-1,2-diphenylethane.—A suspension of 1.80 g. (0.01 mole) of stilbene in a solution of 3.18 g. of mercuric acetate in 50 ml. of methanol was shaken for fifteen days, during which time the concentration of mercuric acetate (estimated by titration with thiocyanate after a 1 ml. aliquot in 8 ml. of water was twice extracted with 5-ml. portions of chloroform) decreased gradually to zero. At this point the mixture contained 1.50 g. (0.007 mole) of mercurous acetate. Evaporated chloroform extracts of the later aliquots gave a mixture melting at 107°. To the reaction flask was added 0.04 mole of mercuric acetate and the mixture was then refluxed (bad bumping) for three days; after cooling it was then filtered to remove mercurous and excess mercuric salt. The filtrate, diluted with water, was extracted twice with chloroform and this solution, dried with magnesium sulfate, was evaporated to leave a gummy residue which, crystallized from ethanol, melted at 139–140° and weighed 0.64 g. Since the substance was demonstrated by mixed melting point and by analysis to be hydrobenzoin dimethyl ether the yield is 26%. A variation in procedure involving immediate heating in a sealed tube to 100° for ninety-six hours gave a much lower yield.

This hydrobenzoin dimethyl ether was obtained in like manner by refluxing 4.47 g. (0.01 mole) of α-chloromercuri-β-methoxy-α,β-diphenylethane from *cis*-stilbene with 6.36 g. (0.02 mole) of mercuric acetate in 50 cc. of methanol for sixty-five hours. The mercurous salt which precipitated during reaction weighed 3.95 g. (80% of the theoretical if 2 equivalents of mercurous salt are formed in the reaction). In addition to 1.53 g. of unchanged mercurial (28% of original amount), there was isolated 0.90 g. of hydrobenzoin dimethyl ether, m. p. 135° (37% of theoretical) which, crystallized from 2:1 ethanol–water, melted at 139–140°. A mixed melting point with a sample prepared by Purdie methoxylation of hydrobenzoin was not lowered.

Low Melting α-Chloromercuri-β-methoxy-α,β-diphenylethane from *trans*-Stilbene.—A solution of 3.18 g. (0.01 mole) of mercuric acetate in 40 cc. of absolute methanol was refluxed with 1.80 g. (0.01 mole) of *trans*-stilbene until solution was complete and then cooled with stirring until the stilbene crystallized to a fine suspension. To this solution was added 0.001 mole of either benzoyl peroxide or ascaridole. This mixture was stirred for one day at room temperature, after which it was filtered (to remove 0.77 g. of stilbene contaminated with mercurous salt) into 50 cc. of 2% sodium chloride solution. The white precipitate which separated was filtered off, washed with water to remove mercuric salt, and dried; weight 2.10 g., m. p. 96–100°. Four washings with 10-cc. quantities of ether removed 0.79 g. of stilbene from this crude product, which now melted at 125–126°. After two crystallizations from 1:9 chloroform–petroleum ether (b. p. 60–70°) the compound melted at 130° (cor.) and weighed 1.05 g. (23.6%). A mixed melting point with the previously known diastereomer melted at 95–100°.

Anal. Calcd. for $C_{15}H_{15}OHgCl$: C, 40.27; H, 3.38; OCH_3, 6.93; Hg, 44.8; Cl, 7.94. Found: C, 40.53; H, 3.43; OCH_3, 6.90; Hg, 44.4; Cl, 7.91.

When one equivalent of boron trifluoride etherate was substituted for the peroxide in an otherwise identical experiment, no mercurial was present at the end of the experiment. This was demonstrated by treating a chloroform solution of the product with an excess of bromine. Stilbene dibromide and hydrobenzoin dimethyl ether subsequently were isolated but no mercuric bromide could be detected.

Acceleration by Peroxides in Formation of α-Acetoxymercuri - β - methoxy - β - phenylpropionitrile.—Ascaridole (0.01 equiv.) catalyzed the reaction until about one-fourth of the mercuric acetate was consumed, after which no further reaction occurred. The reaction proceeded with benzoyl peroxide to the extent of 10% using 0.01 equiv., 25% with 0.1 equiv., 45% with 0.5 equiv., and 65% with 1 equiv. Substantially the same results were obtained with peracetic acid. One equivalent of hydrogen peroxide allowed 50% of the mercuric acetate to be consumed. Dimethyl peroxide (0.1 equiv.) caused an immediate drop of 10% in mercuric acetate concentration; acetone superoxide acted likewise though somewhat more slowly. In every case a test, after the reaction had stopped, showed no peroxide to be present. In no case could the mercurial of styryl cyanide be isolated; instead a chloroform-soluble compound, m. p. 190–210°, was obtained.

Acceleration in Formation of α-Chloromercuri and α-Acetoxymercuri-β-methoxy-β-phenylpropiophenone.—Peroxide-free benzalacetophenone (0.01 mole) with 0.01 mole of mercuric acetate in absolute methanol to a total volume of 50 ml. reacts completely in less than twelve hours, its half-life being approximately sixty minutes, when a centrifuged stock solution (conveniently 0.25–0.28 *M*) of mercuric acetate twice crystallized from dilute acetic acid is used to introduce this salt. The analytical procedure is identical with that outlined previously[2] except that 1-ml. aliquots from the well-mixed 50-ml. flask contents were introduced into 10 ml. portions of water containing 1 ml. of saturated potassium nitrate, and extracted five times with 2-ml. portions of chloroform. The end-point should persist for one minute after titration with 0.1 *N* thiocyanate to the nearest 0.003 ml. using 0.2 ml. of ferric indicator. A badly fading end-point, however, indicates incomplete extraction of organomercurial. In case the potassium nitrate does not fully break the emulsion, the latter should be retained in the upper layer. Upon completion of the reaction the expected mercurial was isolated in 71% yield, m. p. 115°. When 0.2 equiv. of dimethyl peroxide was added to the reactants the half-life was forty-two minutes (Fig. 1, A). With 0.5 equiv. of hydrogen peroxide the half-life was forty-nine minutes but the drop was much greater at first and gradually decreased in rate to this value. This latter result is expected if one examines the fate of mercuric acetate in methanol containing hydrogen peroxide; a decrease in mercuric salt content is observed when the prescribed analytical procedure is used, which reaches its minimum in about one hundred minutes. The apparent mercuric salt content then increases until finally it reaches the initial mercury concentration. The phenomenon seems to be associated with a yellow turbidity which appears and disappears during the reaction. For this reason hydrogen peroxide is unsuitable for rate determinations, although the normal product can be isolated in 71–76% yield using this catalyst.

When 0.1 equivalent of boron trifluoride etherate was used as the catalyst the reaction was complete in eight minutes, only 88% of the mercuric acetate apparently having been consumed. The clear solution was poured into 200 cc. of water and sodium chloride solution was added until coagulation was complete. After twelve hours the precipitate was filtered off, weighing 4.38 g. and melting at 70–75°. After the compound was suspended in a solution of 2.70 g. (0.01 mole) of mercuric chloride in 25 cc. of ethanol for two hours, it was crystallized by heating this medium to yield 3.93 g. of α-chloromercuri-β-methoxy-β-phenylpropiophenone, m. p. 150–151°, or 96%. A mixed melting point with the compound obtained by treating a methanol solution of α-acetoxymercuri-β-methoxy-β-phenylpropiophenone with sodium chloride and twice crystallizing from ethanol to constant melting point of 151° was not lowered.

Anal. Calcd. for $C_{16}H_{15}O_2HgCl$: C, 40.4; H, 3.16. Found: C, 40.7; H, 3.18.

When either the catalyzed or uncatalyzed addition to benzalacetophenone ceased, leaving 10–12% of the mercuric salt uncombined, addition of a second equivalent of benzalacetophenone quickly reduced this value to zero. After four days the resultant solution was poured into water and 2 equiv. of sodium hydroxide solution was added. The resultant gum was taken up in chloroform, dried by vacuum evaporation, and ether was added to precipitate the hydroxymercuri compound (m. p. 172°). The filtered solution yielded, after vacuum evaporation, a gummy semisolid mass which could not be purified.

To a suspension of 4.16 g. (0.02 mole) of benzalacetophenone and 3.18 g. (0.01 mole) of mercuric acetate in 50 ml. of methanol at 25° was added 0.001 mole of boron trifluoride etherate. The suspension dissolved immediately to cool the solution about 10°. After ten minutes, titration showed no uncombined mercuric acetate. After one hour 2.70 g. (0.01 mole) of mercuric chloride in 20 cc. of methanol was added. When this solution was immediately poured into water, a gum appeared which crystallized after one hour; it weighed 7.30 g. and melted at 60–110°. After suspension in alcohol containing 0.01 mole of mercuric chloride for two hours, and subsequent solution in 60 cc. of this medium, 3.73 g. of α-chloromercuri-β-methoxy-β-phenylpropiophenone, m. p. 148°, was obtained.

If instead of pouring the reaction product into water immediately after addition of mercuric chloride, it was allowed to stand overnight, 7.50 g. of the chloromercurial, m. p. 148–149°, crystallized out. The mother liquors, after dilution with water, yielded 1.55 g. of solid, m. p. 60–110°, which when treated with mercuric chloride solution as outlined above yielded 0.95 g. of chloromercurial, m. p. 148°. The total yield, m. p. 148°, is 89% of the theoretical.

Retardation in Formation of α-Chloromercuri- and α-Acetoxymercuri-β-methoxy-β-phenylpropiophenone.—While the purified mercuric acetate reacted within a half-life of sixty minutes, two commercial grades reacted somewhat slower. Mallinckrodt Reagent grade, which smelled strongly of acetic acid, gave a half-life period of one hundred and ten minutes, while British Drug House Analar grade required four hundred minutes for half consumption. Qualitative analysis of the latter reagent gave negative tests for nitrogen and sulfur. In each of these experiments, titration showed that about 10% of mercuric salt remained at the end of the reaction while the yields of chloromercurial obtained by the method outlined above were equal to or greater than 90%.

Some difficulty was encountered in choosing a suitable inhibitor from the known list of antioxidants. Diphenylamine reacted immediately with mercuric acetate. Durene had no effect on rate of addition. Retardation was obtained as follows to give the indicated percentage yields: 1 equiv. acetonitrile: half-life, three hours, 76; 1 equiv. *trans*-styryl cyanide: half-life, three hours, 65; 1 equiv. pyridine: complete, eleven days, 52; 0.1 equiv. pyridine: 5% life, ninety minutes, 52; 0.1 equiv. diethyldisulfide: half-life, five hours, 50.

All but the last of these substances were then qualitatively examined, together with others used in the reaction mixture, for peroxide content, the criterion for presence and amount of peroxide being the time for appearance of a yellow coloration when one drop of the hydrochloric acid-stabilized 2% solution of titanium trichloride was added to 1 ml. of methanol containing the substances listed in Table I.

TABLE I

PEROXIDE CONTENT OF REACTION COMPONENTS

Substance No. 1	Substance No. 2	Time, min.	Color
Methanol	.....	0	−
Methanol	0.02 cc. nitric acid	0	+
Methanol	.02 cc. nitric acid	240	++
Benzalacetophenone	.....	0	−
Styryl cyanide	.....	0	−
0.007 mole styryl cyanide	.0001 mole H_2O_2	240	++++
Acetonitrile	.....	0	−
0.007 mole acetonitrile	.0001 mole H_2O_2	240	++++
Pyridine	.....	0	−
0.007 mole pyridine	.0001 mole H_2O_2	0	++
0.007 mole pyridine	.0001 mole H_2O_2	240	− (?)
Dimethyl peroxide	.....	0	++

Catalytic Effect of Diethyldisulfide.—When 0.01 mole of mercuric acetate in 40 cc. of methanol (freed of mercurous salt by centrifuging) was treated with 1.22 g. (0.01 mole) of diethyldisulfide (Eastman Kodak Co., redistilled) an aliquot subjected to the analytical procedure used in titration of the mercurials gave less than one-tenth the expected titer with thiocyanate. The methanol solution was evaporated to dryness at 10 mm. pressure. The residue was extracted with three 20-cc. portions of chloroform leaving 0.8 g. of impure mercuric acetate. Evaporation of the chloroform solution left a solid, m. p. 127–129°, which when dissolved in chloroform and precipitated with ether melted at 131–132°. Since repetition of this process failed to raise the melting point, it was dried at 25° (8 mm.) for analysis. When dissolved in methanol and precipitated with 5% aqueous sodium chloride a white precipitate, infusible at 260° was formed. Both the acetoxymercuric and chloromercuric salts gave an odor of ethyl mercaptan with hydrochloric acid. The odor disappeared when excess base was added.

Anal. Calcd. for $C_4H_8HgSO_2$: C, 14.95; H, 2.51. Found: C, 14.87; H, 2.53.

When 0.1 equiv. of diethyldisulfide was treated with one equiv. of mercuric acetate in methanol the titration with thiocyanate, using the procedure outlined,[2] was 78% of the calculated value. To allow for this error, 22% of the observed titration value was added to each. The titrations were difficult owing to precipitated material and ephemeral end-point.

Catalytic Effect of Boron Salts.—A boron acetate was prepared by heating 0.16 mole (10 g.) of Merck U. S. P. boric acid under reflux with 50 cc. of acetic anhydride until solution was complete. The solvent was removed at 60° (8 mm.) and the residue was crystallized from 15 cc. of hot acetic acid.

Anal. Calcd. for $C_4H_7O_5B$: C, 32.9; H, 4.78. Found: C, 32.2; H, 4.50.

This compound exerted no catalytic effect on the mercuric acetate–*cis*-styryl cyanide reaction in methanol. In order to ascertain whether fluoride interfered with the thiocyanate titration, 1 ml. of a methanol–mercuric acetate solution which was equivalent to 5.61 cc. of 0.1 *N* thiocyanate was treated with 0.00004 mole of boron trifluoride etherate; the titration equivalence was 5.59 cc. The isomerizing effect of the boron trifluoride was not detectable when 1 cc. of either *cis*- or *trans*-styryl cyanide was treated with 0.0004 mole of the etherate in 10 cc. of methanol. After two days these solutions were poured into 5% sodium carbonate, extracted with ether, dried with calcium chloride and distilled *in toto* at 10 mm. pressure. The distillate from attempted isomerization of *cis*-styryl cyanide had $n^{20}\text{D}$ 1.5840; from *trans* $n^{20}\text{D}$ 1.6031. The catalyst solution for subsequent experiments was prepared by adding methanol cooled to 10° to 7 g. of pract. Eastman Kodak Co. boron trifluoride etherate to make a volume of 25 ml. A 0.5-ml. aliquot of this solution accelerated 50 ml. of a 0.2 molar *cis*-styryl cyanide–mercuric acetate solution to a half-life of ninety-five minutes, but only one-fourth of the *trans*-styryl cyanide reacted under identical conditions and no recognizable product could be isolated. Consequently 0.01 molar (equiv.) quantities of catalyst were used in subsequent experiments.

α - Chloromercuri - β - methoxy - β - phenylpropionitrile. A. From *cis*-Styryl Cyanide.—The acetoxymercurial obtained from *cis*-styryl cyanide[2] (0.12 g., m. p. 121–122°; was dissolved in 2 cc. of ethanol and diluted to 10 cc. with saturated sodium chloride solution. After twelve hours the precipitate was filtered off, washed with water (m. p. 172°), and was crystallized from boiling ethanol (1 g.: 50 cc.) to a constant melting point of 174°.

Anal. Calcd. for $C_{10}H_{10}OHgClN$: C, 30.3; H, 2.55. Found: C, 30.2; H, 2.67.

The compound was prepared from 0.01 mole of *cis*-styryl cyanide, 0.01 mole (3.18 g.) of mercuric acetate and 0.001 mole of boron trifluoride etherate (0.14 g.) in 50 ml. of methanol. The reaction was complete in fourteen hours, the discrepancy between this time and a half-life of ninety minutes becoming apparent in the observation that the second order rate constant dropped off badly after forty minutes. After twelve hours the precipitate was filtered off, weight 3.01 g., m. p. 164–167°. This material, crystallized from ethanol melted at 172–173°; the mixed melting point with material prepared from the acetoxymercurial was not lowered. The yield, 78%, may be somewhat improved by use of an equivalent amount of catalyst.

B. From *trans*-Styryl Cyanide.—When 0.004 mole (1.68 g.) of the acetoxymercurial from *trans*-styryl cyanide, m. p. 90°, was dissolved in 20 cc. of methanol and 75 cc. of a 12% sodium chloride solution was added slowly, the resulting precipitate melted at 58–62° (1.48 g.). Attempts to crystallize this material from hot ethanol caused it to decompose with formation of a gummy intractable mass. If, however, it was dissolved in methanol at 25° together with 0.004 mole (1.08 g.) of mercuric chloride and later diluted with water, the precipitate melted at 120–125°. Crystallization from boiling ethanol (1 g.: 5 cc.), using charcoal, resulted in a constant melting point of 124.5°.

Anal. Calcd. for $C_{10}H_{10}OHgClN$: C, 30.3; H, 2.55. Found: C, 30.1; H, 2.62.

To a solution of 0.01 mole of *trans*-styryl cyanide (1.29 g.) and 0.01 mole of mercuric acetate (3.18 g.) in methanol at 35 ± 0.01° was added 0.01 mole of boron trifluoride etherate (0.14 g.). The reaction followed a second order course smoothly through its half-life of twenty minutes but shortly afterward dropped off badly and appeared to stop entirely at five-eighths life. After two hours the solution was poured into 500 cc. of water and extracted with five 100-cc. portions of chloroform. This chloroform extract was evaporated to dryness *in vacuo* and the residue shaken with a solution of 0.01 mole of mercuric chloride (2.70 g.) and 7 g. of sodium chloride in 200 cc. of water together with a few cc. of chloroform. After the latter was removed by evaporation *in vacuo*, the residual solid was filtered off, m. p. 110–115°, weight 2.56 g. After two crystallizations from ethanol using charcoal it melted at 123–124°, mixed melting point with compound obtained from acetoxymercurial was not lowered. The yield, 1.80 g., was 47% of the theoretical. The aqueous solution, following chloroform extraction, was treated with 2.7 g. of mercuric chloride and 25 cc. of saturated sodium chloride solution and then extracted thrice with chloroform. Evaporation of the latter *in vacuo* left an infusible white solid, soluble in chloroform, which could be precipitated from this solution by addition of ether. It turned slightly yellow on heating with 10% aqueous sodium hydroxide and the odor of styryl cyanide was evolved upon boiling the substance with 12% hydrochloric acid; the residual solution contained inorganic mercury. This infusible material was found to contain 17.11% carbon and 1.62% hydrogen.

When two equivalents of mercuric acetate in a 0.2 *M* methanol solution was treated with one equivalent of *trans*-styryl cyanide and one equivalent of boron trifluoride etherate at 35°, the reaction ceased when 34% of the original mercuric salt could still be titrated. None of the normal addition product could be isolated from this experiment.

2,3-Dibromo-3-phenylpropionitrile.—A solution of 0.01 mole of *trans*-styryl cyanide in 5 cc. of chloroform was treated with 0.01 mole of bromine; it required four days before the color disappeared. Evaporation at 12 mm. left a crystalline residue which was crystallized from a mixture of 15 cc. of petroleum ether (b. p. 60–70°) and 5 cc. of ether to yield 1.77 g., m. p. 92–93°. This was crystallized from 4 cc. of ethanol to the same melting point.

Anal. Calcd. for $C_9H_7Br_2N$: Br, 55.4. Found: Br, 55.7.

When 0.01 mole of *cis*-styryl cyanide was treated in like manner, much hydrogen bromide was evolved over a three-day period. After removal of the solvent a semi-crystalline mass remained from which, by extraction with ether, a white solid, m. p. 202°, was left behind. The ether solution after evaporation left a pasty crystalline mass from which 0.47 g. of the dibromide described above could be isolated from a porous tile.

The authors wish to thank Miss Joan Romeyn and Miss Gladys Stonestreet for aid in the microanalyses.

Summary

1. Three concomitant reactions occurring during addition of the methoxymercuric acetate elements to ethylenes have been observed, two of which have been identified as oxidation to the dimethoxyethane and as dismutation to the diorganomercury derivative.

2. Nitriles, pyridine, diethyldisulfide and an unidentified impurity in mercuric acetate have been found to retard the addition reaction.

3. The reaction is accelerated by peroxides, and by boron trifluoride etherate.

TORONTO, ONTARIO RECEIVED JUNE 22, 1940