

### Summary

1. A series of simple mercurated azo dyes containing solubilizing groups has been prepared from *o*-chloromercuriphenol and 2,6-diacetoxymercuri-*p*-cresol with diazotized solutions of the following acids: sulfanilic, metanilic naphthionic, anthranilic, *m*-aminobenzoic and *p*-aminobenzoic.

2. The stability of the C—Hg linkage is found to remain essentially the same as in the parent compounds.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## THE IRREVERSIBLE REDUCTION OF ORGANIC COMPOUNDS II. THE DIMOLECULAR REDUCTION OF CARBONYL COMPOUNDS BY VANADOUS AND CHROMOUS SALTS

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Several investigations have been carried out in this Laboratory in the past few years in order to discover to what extent it is possible to formulate the reduction of organic substances in electrochemical terms.<sup>1</sup> Attention has been centered on homogeneous systems in order to avoid the complications of diffusion processes and, therefore, such soluble reducing agents as stannous, titanous, vanadous and chromous salts have been employed. The irreversible reduction of most azo and nitro compounds, unsaturated 1,4-diketones (and related compounds) and 1,2-diketones can be readily accomplished by titanous chloride or some reducing agent of even higher potential (for example, stannous chloride).<sup>2</sup> Since chromous chloride is the most powerful soluble reducing agent known ( $\pi_0 = -0.4$  volt), we have been interested in determining its action on various classes of organic compounds which are not reduced by the more usual soluble reducing agents.

Berthelot<sup>3</sup> discovered that acetylene was reduced to ethylene by ammoniacal chromous chloride. Traube and Passarge<sup>4</sup> showed that the same process occurred in acid solution and that fumaric and maleic acids were reduced by chromous chloride.<sup>5</sup>

<sup>1</sup> (a) THIS JOURNAL, **44**, 1382, (b) 2480 (1922); (c) **45**, 1047, (d) 2194 (1923); (e) **46**, 1254, (f) 1858 (1924); (g) *J. Phys. Chem.*, **28**, 1096 (1924).

<sup>2</sup> For the quantitative formulation of such processes see THIS JOURNAL, **46**, 1254 (1924) and **45**, 1048 (1923).

<sup>3</sup> Berthelot, *Ann. chim.*, [4] **9**, 401 (1866).

<sup>4</sup> Traube and Passarge, *Ber.*, **49**, 1692 (1916).

<sup>5</sup> These authors also carried out experiments with alkaline suspensions of chromous hydroxide. Since one must here consider the possibility of reduction on an active surface, experiments with this reagent do not lend themselves to precise electrochemical treatment.

We have found that solutions of chromous chloride in acidic aqueous or alcoholic solution are *without effect* at room temperature on representative *aliphatic* or *aromatic saturated ketones*, *aliphatic aldehydes*,  $\alpha,\beta$ -*unsaturated acids* and *esters*, *alcohols* (with the exception of certain aromatic carbinols mentioned below), and olefin *hydrocarbons*. The color change from the bright blue chromous salt to the dark green chromic salt was found to be a serviceable and reliable criterion of whether or not reduction had occurred. Quantitative electrometric titrations were also employed in many cases; the details of these experiments are given in the experimental portion of this paper.

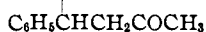
On the other hand, *many  $\alpha,\beta$ -unsaturated ketones and aldehydes and aromatic aldehydes are reduced* with the formation of *dimolecular products*. In this and other respects the process differs from the reduction of com-

pounds containing the groups  $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C}-\text{C}- \end{array}$  or  $\begin{array}{c} \text{O} \quad \quad \quad \text{O} \\ \parallel \quad \quad \quad \parallel \\ -\text{C}-\text{C}=\text{C}-\text{C}- \end{array}$  and is analogous to the dimolecular reduction of aryl carbinols in acid solution. Recent<sup>6</sup> studies in this Laboratory have shown that this reduction of aryl carbinols proceeds through the halochromic salt and involves the formation of free radicals with trivalent carbon. As will be shown below, the action of chromous or vanadous salts on aldehydes or ketones can be satisfactorily formulated in similar terms.

### $\alpha,\beta$ -Unsaturated Ketones

Benzal-acetophenone ( $\text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5$ ), benzal-acetone ( $\text{C}_6\text{H}_5\text{CH}=\text{CHCOCH}_3$ ), ethylidene-acetone ( $\text{CH}_3\text{CH}=\text{CHCOCH}_3$ ), benzal-acetomesitylene ( $\text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_2(\text{CH}_3)_3$ ), cinnamylidene-acetophenone ( $\text{C}_6\text{H}_5\text{CH}=\text{CH}-\text{CH}=\text{CHCOC}_6\text{H}_5$ ), and dibenzal-acetone ( $\text{C}_6\text{H}_5\text{CH}=\text{CHCOCH}=\text{CHC}_6\text{H}_5$ ) were reduced rapidly by alcoholic chromous chloride. Dypnone ( $\text{C}_6\text{H}_5(\text{CH}_3)\text{C}=\text{CHCOC}_6\text{H}_5$ ) was reduced more slowly and mesityl oxide ( $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$ ) was not reduced even after three days.

The products of reduction were amorphous, white precipitates which separated from the solutions and carried down considerable quantities of unchanged ketone; as yet, we have examined only the products from benzal-acetone and benzal-acetophenone. From benzal-acetone the dimolecular product (I) described by Harries<sup>7</sup> was isolated, and from benzal-acetophenone two stereoisomeric substances (II), the higher melting of which



I



II

<sup>6</sup> THIS JOURNAL, 47, 1959 (1925).

<sup>7</sup> Harries, *Ber.*, 29, 212, 381 (1896).

was obtained by Harries by reduction with zinc and acid. The lower-melting isomer when treated with sodium ethylate undergoes the characteristic internal condensation of 1,6-diketones, forming a cyclopentene ketone. Both isomers when treated with bromine in acetic acid yield the same yellow compound,  $C_{30}H_{22}OBr_2$ , with evolution of hydrogen bromide. The structure of this substance has not yet been established but its formation from both the reduction products indicates that they are stereo- and not structural isomers. The formation of a few per cent. of the high-melting isomer during distillation of the low-melting substance in a vacuum is further evidence in this direction.

The reduction of benzalacetophenone was studied in some detail in order to determine the best conditions for obtaining crystalline products and to determine whether or not monomolecular products were formed. The use of aqueous solutions of vanadous salts instead of chromous salts was found to be equally effective and more convenient. A hot alcoholic solution of the ketone could be added to a solution of acidic vanadous sulfate or a solution of vanadous chloride added to an acetone solution of the ketone. The second procedure is preferable, and in this way the following yields were obtained: 45% of low-melting dimolecular product, 35% of high-melting product, 10% of unchanged ketone (isolated as the dibromide after treatment with bromine) and 10% of non-crystalline oils. The amount of monomolecular reduction product, if any, must therefore have been less than 10%. The non-crystalline oils (10%) may have consisted largely or in part of a dimolecular reduction product formed by pinacone reduction of the carbonyl group instead of the conjugated system. However, the following equation represents the transformation of *at least* 90% of the material.  $2C_6H_5CH=CHCOC_6H_5 + 2V^{++} + 2H^+ \longrightarrow (C_6H_5CHCH_2COC_6H_5)_2 + 2V^{+++}$ .

### Aromatic and Unsaturated Aldehydes

Benzaldehyde, anisaldehyde, piperonal and dimethyl-aminobenzaldehyde are slowly reduced both by chromous and vanadous salts in the presence of acid and enough alcohol or acetone to produce a homogeneous solution. Electrometric titrations of the amount of chromous ion which was oxidized in the reduction of benzaldehyde by alcoholic chromous chloride showed that a dimolecular (pinacone) reduction had taken place. The product was a thick oil containing some halogen which fact indicated that secondary reactions involving hydrogen chloride were perhaps involved. By using aqueous acidic vanadous sulfate and sufficient alcohol to keep the benzaldehyde in solution, a crystalline mixture of hydrobenzoin and isohydrobenzoin was obtained which corresponded to somewhat more than a 90% yield. The mixture was identified by oxidation to benzil. No trace of benzyl alcohol or toluene was found in the reaction product;

the reaction is therefore,  $2C_6H_5CHO + 2V^{++} + 2H^+ \longrightarrow (C_6H_5CHOH)_2 + 2V^{+++}$ .

The results with the unsaturated aldehydes were less satisfactory, for a considerable amount of the material was converted into products which could not be obtained pure or identified. These were for the most part very high boiling non-crystalline substances. The pinacone reduction products (III) previously obtained by reduction with a zinc-copper couple<sup>8</sup> were isolated and identified in the following yields: from acrolein (R=H), 30%; from croton aldehyde (R=CH<sub>3</sub>), 18%; from cinnamic aldehyde (R=C<sub>6</sub>H<sub>5</sub>), 5%. A careful search was made for monomolecular reduction



products, which should have been easily separable by distillation from the dimolecular products. A very faint test for *n*-propyl aldehyde was given by the distillate containing the unchanged acrolein in an experiment with this aldehyde, but aside from this no evidence of monomolecular reduction was obtained. It is fairly certain that no products were obtained of Type IV (or the cyclopentene aldehyde formed by the inner condensation of IV), since no substances forming bisulfite addition compounds were found.

As a preparative procedure the reduction of unsaturated aldehydes with vanadous salts is much less satisfactory than with a zinc-copper couple. With acrolein the best result was obtained by using a solution of vanadous sulfate heptahydrate (VSO<sub>4</sub>·7H<sub>2</sub>O) (prepared electrolytically) in water without the addition of acid (a brown solution). When reduction was carried out with a vanadous solution containing zinc sulfate and sulfuric acid (purple solution), 27% of the material was converted into a liquid insoluble in water (b. p., 167–168°) whose analysis corresponded to the formula C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>; its structure has not been established.

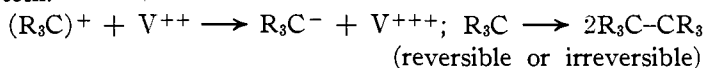
It was thought that this oil might be formed by the action of the acid on the divinylglycol but the liquid in question was not formed, although the glycol is changed by treatment with acid. On the other hand, experiments with dipropenylglycol indicated that some of the products of the reduction of crotonaldehyde were formed by a secondary action of the acid on the unsaturated glycol.

In spite of the complications of side reactions, it appears that the chief reaction with unsaturated aldehydes is as follows:  $2RCH=CHCHO + 2V^{++} + 2H^+ \longrightarrow (RCH=CH-CHOH)_2 + 2V^{+++}$ .

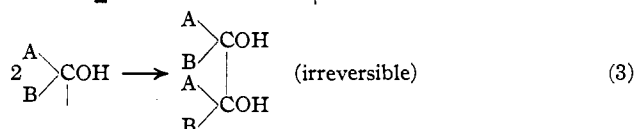
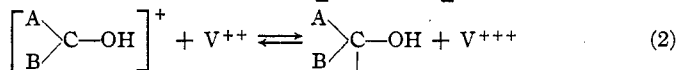
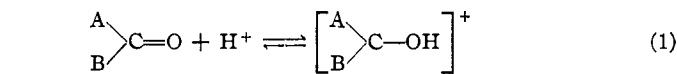
<sup>8</sup> Griner, *Ann. chim. phys.*, [6] **26**, 369 (1892). Charon, *ibid.*, [7] **17**, 197 (1899). Thiele, *Ber.*, **32**, 1296 (1899).

### Mechanism of the Reaction

Carbonyl compounds in the presence of acids form salts closely allied to the halochromic salts of the aryl carbinols as Hantzsch<sup>9</sup> has demonstrated. Thus if the aryl carbinols  $R_3COH$  are weak pseudo bases in relation to the salts  $(R_3C)X$  the unsaturated ketones and aldehydes  $RCH=CH-\overset{R}{C}=O$  are weak anhydro bases of the salts  $(RCH=CH-\overset{R}{C}-OH)X$ . It has been shown that the interaction of the salts of aryl carbinols and reducing agents results in the formation of free radicals containing trivalent carbon which either reversibly or irreversibly polymerize<sup>10</sup> to ethanes according to the nature of the groups attached to the central carbon atom.



The interaction of reducing agents and a carbonyl compound  $\begin{matrix} A \\ \diagdown \\ C=O \\ \diagup \\ B \end{matrix}$  (where A =  $C_6H_5$  or an  $\alpha,\beta$ -unsaturated group, and B = H or  $C_6H_5$ ) can be formulated in an analogous manner.



In the case of the unsaturated ketones, the polymerization must be considered as involving the beta carbon atom instead of the carbonyl carbon atom, and the "free radical" might be written:  $C_6H_5CH-CH=C-C_6H_5$

or  $C_6H_5CHCH_2COC_6H_5$ . Moreover, if one cares to consider the positive charge as localized at a particular point on the organic ion, the

formula  $C_6H_5\overset{+}{C}H-CH=COHC_6H_5$  or  $C_6H_5\overset{+}{C}HCH_2COC_6H_5$  would represent the behavior of benzal-acetophenone in contrast to cinnamic aldehyde

whose ion would be written as  $C_6H_5CH=CH-\overset{+}{C}HOH$ . Tautomerization of polar and odd molecules (free radicals) occurs so frequently, however,

<sup>9</sup> *Ber.*, **55**, 953 (1922). See also Scheibe, *Ber.*, **58**, 586 (1925).

<sup>10</sup> *THIS JOURNAL*, **47**, 1959 (1925).

that we prefer for the present to write the halochromic salt in the Wernerian manner.

From a consideration of Reactions 1, 2 and 3 it is evident that the speed of either Reaction 2 or 3 will control that of the entire process since the rate of salt formation is presumably so rapid as to be negligible. In both cases, at a constant acidity, the reaction will be apparently dimolecular as regards the effect of dilution on the fraction reacted. This we have found to be the case with benzaldehyde and cinnamic aldehyde in an acetone-acetic acid solution with vanadous chloride; the experiments will be reported in detail in a later paper.

Since the speed of Reaction 2 is a function of the acidity of the solution

$$\text{rate(s)} = k K [V^{++}] [\text{ketone}] [H^+] \quad (4)$$

where

$$\frac{[\text{org. ion}]}{[\text{ketone}] [H^+]} = K$$

(Equation 4), with decreasing acidity it will become eventually the controlling factor and the speed of the entire process will then be controlled by the acidity of the medium. Under such conditions equilibrium will not be reached in Step 2. At a sufficiently low acidity the process will become too slow to be measurable. This we have found to be the case qualitatively in the reduction of benzaldehyde with chromous or vanadous salts. The fact that the alkaline reducing agent sodium hydrosulfite  $Na_2S_2O_4$  will not reduce the compounds in question is also in accord with this formulation. The difficulty of finding suitable "buffer solutions" in which the organic material and the vanadous salt are soluble has delayed our study of the quantitative aspects of this problem. We hope, however, to deal with the kinetics of the reaction in a later paper. Preliminary measurements in acetone solutions indicate the correctness of our interpretation.

It should be noted that if the potential of the reducing agent employed is high in comparison to that of the organic system ( $[ABCOH]^+ - ABCOH$ ) (that is, a "weak" reducing agent) very little free radical will be present at equilibrium and the rate of Reaction 3 will be consequently slow and the governing process. In this instance we are concerned with a reaction whose rate is controlled by an equilibrium process just as in the case of the irreversible reduction of unsaturated 1,4-diketones, azo compounds, etc.,<sup>1</sup> except that the process is dimolecular. The possibility of formulating these dimolecular reductions under certain conditions in terms of "apparent reduction potentials" will be considered in another paper.

Just as the reduction of aryl carbinols in acid solution is not really a reduction of the carbinol but of a transformation product—the halochromic salt, so we believe the dimolecular reduction of carbonyl compounds by soluble reagents is not a direct reduction of the carbonyl group, but of its addition product with the hydrogen ion. If this is true, the dimolecular reduction of the carbonyl compounds is in sharp contrast to the reversible

and irreversible reduction of compounds containing 1,2- and 1,4-diketone groups. There is no evidence to indicate that the speed of reduction of such substances is a function of the hydrogen ion concentration. It seems hardly possible that the very rapid reduction of anthraquinone sulfonate by sodium hydrosulfite, for example, proceeds through an ion of the type  $AH_2^{++}$  or  $AH^+$  in strongly alkaline solution ( $A$  = anthraquinone molecule),<sup>11</sup> or that the irreversible reduction of dibenzoyl-ethylene in alkaline solution proceeds through halochromic salts. Neither anthraquinone nor dibenzoyl-ethylene behaves as a strong anhydro base and the amount of halochromic salt of a weak base at  $[H^+] = 10^{-12}$  must be very minute indeed.

It is much more probable that we are here dealing with two distinctly different processes; (1) the reduction of ions (from pseudo bases, real bases,<sup>12</sup> or anhydro bases), and (2) the reduction of particular types of doubly unsaturated systems which can directly capture two electrons and subsequently (if necessary) two hydrogen ions. Apparently the simple carbonyl group and the conjugated group  $C=C-C=O$  cannot acquire two electrons from *soluble reducing agents*. Such systems may be able to take up two electrons from a cathode or metallic surface, and the monomolecular reduction of ketones, etc., may often proceed in this way. Heterogeneous monomolecular reduction, however, may also proceed by the direct addition of activated hydrogen atoms, which process cannot be formulated in electrochemical terms as has been shown elsewhere<sup>13</sup> in a discussion of catalytic hydrogenation. The results of the present work give us no direct information on this point, nor on the mechanism of heterogeneous reduction in general. They tend to confirm, however, the hypothesis of Cohen<sup>13</sup> and Steinkopf<sup>14</sup> that the formation of pinacones by metallic reduction in many cases proceeds through a free radical. In the case of acid mediums, it would seem probable, from our results, that the interaction of the halochromic salt and the metal was involved. However, in many cases in neutral or alkaline solution (such as the usual procedure for preparing pinacone from acetone) the mechanism must be entirely different and indeed there is evidence that metallic derivatives of the pinacones are here formed.

It is of interest that we have found the same type of product that was obtained by metallic reduction in the case of those compounds containing the conjugated system with a possibility of 1,2- and 1,4-addition. Kohler's

<sup>11</sup> Compare W. M. Clark, *Pub. Health Repts.*, **38**, 683 (1923), for a discussion of the mechanism of the *reversible* processes.

<sup>12</sup> Compare the reduction of pyridinium salts: Conant and Sloan, *THIS JOURNAL*, **45**, 2466 (1923).

<sup>13</sup> Cohen, *Rec. trav. chim.*, **38**, 72, 113 (1919), and earlier papers. Monomolecular reduction in *alkaline* solution is due to the subsequent cleavage of the pinacone, according to this investigator.

<sup>14</sup> Steinkopf, *Ann.*, **430**, 113 (1923).

results<sup>15</sup> with the Grignard reagent show that this reagent attacks the carbonyl group in unsaturated aldehydes and almost exclusively the conjugated system in benzal-acetophenone. However, the introduction of a second substituent in the  $\beta$ -carbon atom of the unsaturated ketone favors 1,2-addition, presumably because the conjugated system is now less active than the carbonyl group. The fact that dypnone is slowly reduced and mesityl oxide not at all by chromous chloride is evidently closely related to Kohler's observations. An "inactivation" of the conjugated system would retard the reduction, since simple ketones are not attacked by our reagent. It is impossible to say at present whether this loss of "activity" of the conjugated system is to be formulated as a shift in the equilibrium of Reaction 1 or 2.

Pyruvic acid ( $\text{CH}_3\text{COCO}_2\text{H}$ ) and benzoylformic acid are reduced by chromous chloride and the titration of the amount of reducing agent involved shows that unlike benzil and other substances containing the

linkage  $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C}-\text{C}- \end{array}$ , the reduction is bimolecular. We have not as yet isolated the products, but in as much as Steinkopf<sup>14</sup> has recently prepared diphenyl-tartaric acid by the action of zinc and acid on benzoylformic acid, there is little doubt of pinacone formation in this instance. This enhanced activity of the carbonyl group in the alpha position to a carboxyl group is in accord with the other properties of  $\alpha$ -ketonic acids.

## Experimental Part

### Preparation of Reagents

**Chromous Chloride.**—The aqueous solution of chromous chloride used in this work (0.8 to 1.5 *N*) was prepared by the reduction of chromic chloride by amalgamated zinc and hydrochloric acid. It was either kept over amalgamated zinc or filtered through glass wool in an atmosphere of carbon dioxide; if the solution is filtered from suspended material and the acidity is not too high, it will keep for many months without the evolution of hydrogen. The alcoholic solutions of chromous chloride were prepared by the action of zinc on a solution of chromic chloride in alcohol containing some hydrochloric acid. For example, 100 g. of chromic chloride (green) was dissolved in 700 cc. of 95% alcohol and 150 cc. of concd. hydrochloric acid, 80 g. of a high grade of granulated zinc was then added and the reduction allowed to continue in an atmosphere of carbon dioxide in a suitable container. After about four hours the reduction was complete. Such a solution if carefully filtered will keep for several weeks but is considerably more unstable than an aqueous solution.

**Vanadous Chloride and Sulfate** were prepared by the reduction of vanadium pentoxide by amalgamated zinc and acid. Although this procedure involves the sacrifice of considerable zinc and gives a solution containing a large amount of zinc sulfate or chloride, it is very convenient. In certain experiments we employed a solution of vanadous sulfate prepared electrolytically by the reduction of the blue vanadyl sulfate. A typical procedure for the reduction of vanadium pentoxide to vanadous

<sup>15</sup> Kohler, *Am. Chem. J.*, **38**, 511 (1907).



chloride is as follows. Sixty g. of vanadium pentoxide (about 95% pure) was placed in a 1-liter flask equipped with a gas outlet tube dipping under water and covered with 250 cc. of water and 250 cc. of concd. hydrochloric acid. About 90 g. of amalgamated zinc (of high purity) was added and the mixture allowed to stand for 12 hrs. when a brown solution had formed. A further quantity of concd. hydrochloric acid (200 cc.) was then added and after 24 hours the reduction was complete, a clear purple solution resulting. The solution may be kept over amalgamated zinc or filtered into a suitable container in an atmosphere of nitrogen. Solutions of vanadous salts in the absence of mineral acid are brown, so that the purple solution in the course of weeks may become brown due to the gradual using up of the hydrochloric acid by the excess of zinc; the addition of a little concd. hydrochloric acid restores the purple color. Such purple solutions were used in this work unless otherwise stated; they were about molar in vanadous ion.

### Experiments without Isolation of Products

In order to determine what substances were reduced by chromous chloride a great many experiments were performed with representatives of different types of organic compounds. Aqueous chromous chloride or alcoholic chromous chloride was employed, the latter when the organic substance was not sufficiently soluble in water. The procedure in the quantitative experiments was to introduce a weighed amount of organic substance into about 75 cc. of the chromous chloride (about molar), sufficient organic substance being taken to react with all of the chromous salt even if two hydrogen equivalents were involved. A sample of the chromous chloride was added to a standard ferric chloride solution before the introduction of the organic material and a similar sample after the mixture had stood for a definite time (usually 24 hours). The ferrous ion was determined by electrometric titration and thus also the concentration of chromous ion in the original solution and after the elapsed time. Making due allowance for the dilution caused by the introduction of the organic material (usually dissolved in 15 cc. of water or alcohol), it was apparent whether or not any reduction had occurred and, if so, how much. The experiment required a special apparatus, of course, as all the manipulations were performed in an atmosphere of carbon dioxide. The error was about 5%.

In a certain number of cases the change of color of the chromous solution (from blue to green) was taken as the criterion of whether or not reduction had occurred. A solution of the organic material and the chromous solution were mixed in an atmosphere of carbon dioxide and allowed to stand for 24 hours. A small amount (10-15%) of reduction would probably not be detected by this method.

In the following summary (+) indicates that reduction took place within 24 hours (usually at once), the number of equivalents of hydrogen involved as determined by the titration being given in brackets. The sign (-) indicates no appreciable reduction after 24 hours; the asterisk indicates that the result is based on the presence or absence of a color change, all the other results being based on titrations.

**Results.** (a) ALDEHYDES.—In aqueous chromous chloride, formaldehyde (—), acetaldehyde (—). In alcoholic chromous chloride, propionaldehyde (—),\* *n*-heptylaldehyde (—), *n*-butylaldehyde (—),\* phenylacetaldehyde (—),\* benzaldehyde (+) [1], anisaldehyde (+) [1 equiv.] *p*-dimethylaminobenzaldehyde (+), piperonal (+).

(b) KETONES.—In aqueous chromous chloride: acetone (—), methyl-ethyl ketone (—), methylisopropyl ketone (—), diethyl ketone (—), cyclohexanone (—), pyruvic acid (+) [1 equiv.]; benzoylformic acid (+) [1 equiv.]. In alcoholic chromous chloride: *tert*-butylmethyl ketone (—), acetophenone (—), benzophenone (—), benzylphenyl ketone (—),\* dibenzyl ketone (—),\* Michler's ketone (—),  $\beta$ -phenylethylphenyl ketone (—),\* benzil (+) (benzoin isolated), anisil (+) (anisoin isolated), dibenzoylmethane (—), benzoin (—).

(c) UNSATURATED ALDEHYDES AND KETONES.—In alcoholic chromous chloride: ethylidene-acetone (+)\*, benzalacetone (+), benzal-acetophenone (+), benzal-acetomesitylene (+)\* (white ppt. formed), dypnone (+)\* (slow color change and formation of white ppt.), mesityl oxide (—), cinnamic aldehyde (+),\* acrolein (+)\* (in water), crotonaldehyde (+).

(d) ACIDS, ALCOHOLS, UNSATURATED HYDROCARBONS.—In aqueous chromous chloride: formic acid, acetic acid, *n*-butyric acid, phenylacetic acid, benzoic acid, phthalic acid (—),\* cinnamic acid (—)\* (recovered unchanged), dimethylacrylic acid (—),\* maleic acid (+) [2 equiv.], fumaric acid (+) (quantitative yield of succinic acid); methyl, ethyl, *n*-butyl, *tert*-butyl alcohols (—),\* ethylene (—).\* In alcoholic chromous chloride: cinnamic ester (—),\* benzyl alcohol (—),\* *tert*-butyl alcohol (—), diphenylcarbinol (—) (see, however, Ref. 2 for the very slow reduction of this substance in the presence of much acid), triphenylcarbinol (+) (see Ref. 2), diphenylbutadiene (—),\* stilbene (—).\*

### Isolation of Reduction Products from Unsaturated Ketones and Aldehydes

**Benzalacetone.**—Twenty g. of benzalacetone was reduced by treatment of an alcoholic solution with an excess of alcoholic chromous chloride. A white, gummy precipitate formed and was filtered off. On washing with hot alcohol, 5 g. of crystalline material (m. p., 161°) was obtained. This corresponded to the product described by Harries.<sup>16</sup>

**Benzal-acetophenone.**—The use of alcoholic chromous chloride resulted in the formation of a great deal of non-crystalline material as well as the two crystalline products described below, so that the use of vanadous sulfate with alcohol or chromous chloride with acetone is to be preferred. The two procedures are briefly described below.

(A) To a purple vanadous sulfate solution (prepared from 50 g. of vanadium pentoxide by reduction with sulfuric acid and amalgamated zinc) containing an excess of acid (about 6 *N*) was added a solution of 57 g. of benzal-acetophenone in 300 cc. of warm alcohol. After the ketone was added, stirring was continued for one hour and the heavy

<sup>16</sup> Harries, *Ber.*, 29, 381, 2121 (1896).

white precipitate which had formed was filtered off; on drying, it weighed 70 g. By extracting thrice with 300 cc. of boiling acetone most of the non-crystalline material was removed and the residue (18 g.) melted at 258–260°. After one recrystallization from chloroform it melted at 266° (uncorr.). It corresponds to the product described by Harries.<sup>17</sup> The acetone extracts were evaporated to small volume, poured into water and the oily material was extracted with ether. On standing, the ethereal solution deposited 14 g. of a white solid, m. p. 182–187° (see below). On evaporation, 33 g. of a thick, yellow oil resulted which yielded no more crystalline material. Ten g. of this oil in acetic acid decolorized a little more than 7 g. of bromine (without evolution of hydrogen bromide) and 14 g. of benzal-acetophenone dibromide was obtained in working up the product (equivalent to 7.9 g. of unsaturated ketone). The residue of dark tar weighed 3 g.

(b) A solution of 20 g. of benzal-acetophenone in 500 cc. of acetone and 75 cc. of concd. hydrochloric acid was placed in a flask equipped with a stirrer, and a solution of vanadous chloride was slowly added. The vanadous chloride was prepared as described above from 20 g. of vanadium pentoxide, 20 g. of amalgamated zinc, 65 cc. of water and 110 cc. of concd. hydrochloric acid. During the addition of the vanadous solution a white precipitate slowly formed in the green liquid and before the addition was complete the solution became brown. At this point 25 cc. more of hydrochloric acid and 100 cc. of acetone were added. After all of the vanadous solution had been added, the stirring was continued for 45 minutes and finally the mixture was allowed to stand for 12 hours. The white precipitate was filtered off, washed with water and treated as described above under (A). In this way 7 g. (35% yield) of high-melting product and 9 g. (45% yield) of low-melting isomer were obtained. The yellow non-crystalline residue was shown by treatment with bromine to consist of about equal parts of unchanged benzal-acetophenone and an unknown non-crystalline material.

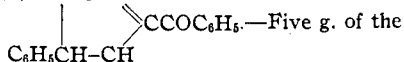
**$\alpha,\delta$ -Dibenzoyl- $\beta,\gamma$ -diphenylbutane (Low-melting Isomer)**,  $C_6H_5COCH_2CH(C_6H_5)CH(C_6H_5)CH_2COC_6H_5$ .—The low-melting isomer obtained as described above after several recrystallizations from acetic acid and finally from ligroin melted at 194°. It distilled at about 360° (5 mm.) with some decomposition and residue; the distillate consisted of the 194° isomer and a few per cent. of the isomer melting at 266°.

*Anal.* Calcd. for  $C_{30}H_{26}O_2$ : C, 86.1; H, 6.2. Found: C, 86.0; H, 6.3.

Bromination of the compound in glacial acetic acid at 80–90° proceeded with evolution of hydrogen bromide. The product was a yellow solid which after recrystallization from acetic acid melted at 171°. The same product was obtained, together with a colorless dibromide, by brominating the high-melting isomer in acetic acid.

*Anal.* Calcd. for  $C_{30}H_{22}OBr_2$ : C, 64.5; H, 4.0; Br, 28.7. Found: C, 65.1; H, 3.8; Br, 28.7.

**2,4,5-Triphenyl-1-benzoylcyclopentene (1,2)**,  $CH_2-C-C_6H_5$



Five g. of the isomer melting at 194° was suspended in 150 cc. of 95% alcohol, and 2 g. of sodium dissolved in ethyl alcohol (sodium ethylate) was added. The mixture was heated to boiling for ten minutes and then allowed to stand for 12 hours. The clear solution was neutralized with acetic acid and evaporated. Four g. of material was obtained which after recrystallizing from alcohol melted at 123°.

*Anal.* Calcd. for  $C_{30}H_{24}O$ : C, 90.0; H, 6.0. Found: C, 90.1; H, 6.0.

**2,4,5-Triphenyl-1-benzoylcyclopentane**.—One g. of the cyclopentene compound

<sup>17</sup> Harries, *Ann.*, **296**, 329 (1897).

was boiled for three hours with zinc dust and acetic acid. The product was isolated in the usual manner and 0.4 g. of a colorless solid, m. p. 148–151°, and some unchanged material were obtained.

*Anal.* Calcd. for  $C_{10}H_{12}O$ : C, 89.7; H, 6.5. Found: C, 89.5; H, 6.5.

**Reduction of Anisaldehyde.**—Twenty g. of anisaldehyde was dissolved in 50 cc. of alcohol, and 220 cc. of an alcoholic solution of chromous chloride (about 0.5 *M*) was added in an atmosphere of carbon dioxide. After 24 hours the solvent was evaporated in a vacuum and the residue treated with water and ether. The unchanged aldehyde (about 12 g.) was removed by shaking the ether layer with bisulfite. From the ether layer 6 g. of white crystals of isohydro-anisoin melting at 98–101° was obtained; after recrystallization they melted at 101°.

**Reduction of Benzaldehyde.**—Benzaldehyde was reduced by alcoholic chromous chloride, and the course of the reaction followed by titrations as described above. Many experiments were carried out under various conditions of concentration. The titrations all showed clearly that a comparatively slow reduction was taking place, going to completion in between 24 and 40 hours, depending upon the experimental conditions. An increase in the acid content of the solution greatly increased the velocity of reduction, dilution caused a slower reaction, while increase of either chromous or aldehyde concentration considerably increased the reaction velocity. Many attempts were made to obtain quantitative information as to the course of the reaction, but because of the impossibility of determining accurately the relative acidity (that is, the hydrogen-ion activity) of the solution no satisfactory results could be obtained.

The titration experiments indicated that when the reaction had gone to completion one atom of hydrogen per mole of aldehyde had been used up. Consequently, the products were probably dimolecular. Preliminary experiments, involving the reduction of benzaldehyde by alcoholic chromous chloride showed that up to 40% of the product was a thick oil which contained halogen and refused to crystallize. As it contained halide, it was probably in part a secondary product formed by the action of hydrochloric acid upon one of the primary products of the reaction. Accordingly, vanadous sulfate was chosen as the reducing agent.

A solution of vanadous sulfate was prepared by the reduction of 60 g. of vanadium pentoxide by sulfuric acid and amalgamated zinc. The solution was diluted to 500 cc., and 400 cc. of alcohol added. The solution was placed in a 2-liter round-bottom flask previously well swept out by carbon dioxide and fitted with a mechanical stirrer. A rapid stream of carbon dioxide from a Kipp generator was kept running through the apparatus. Just 50 g. of benzaldehyde was dissolved in 100 cc. of alcohol and slowly added to the vanadous sulfate solution. The addition took about one hour, the solution being rapidly stirred during the addition. After the aldehyde was all added the stirring was continued for one hour more, and the solution then allowed to stand overnight.

The next morning, considerable white solid was seen in the solution. This was filtered off and dried; weight, 15 g.; m. p., 90–107°. The solution was placed in a distilling flask and about 300 cc. of alcohol distilled under reduced pressure. The main solution was cooled and extracted thrice with 300cc. portions of ether. The ether layers were washed with sodium bicarbonate and water, and evaporated to about 100 cc. The residue was shaken with 100 cc. of saturated sodium bisulfite solution to remove any unchanged aldehyde. No solid product was formed, and no aldehyde was obtained on working up the bisulfite solution. A white solid separated, on evaporating the ether solution, which weighed 19 g.; m. p., 70–110°. Further evaporation yielded 12 g. more of the same solid. No benzaldehyde, benzyl alcohol or toluene could be found in the original alcoholic distillates. The combined solids recovered represented more than 90% of the original aldehyde.

The solid product was recrystallized from alcohol, and melted at 98–110°. Several recrystallizations from alcohol and alcohol-water mixtures did not serve to effect a further purification. The crystals, under a microscope, were easily seen to consist of a mixture of two compounds, one crystallizing in needles and one in little plates.

A few of the plates were separated mechanically from the rest, and recrystallized from a little alcohol. A product melting at 131–133° resulted. This was shown by a mixed melting point to be hydrobenzoin. The needles, similarly treated, melted at 117–118°.

The solid was undoubtedly a mixture of hydrobenzoin and isohydrobenzoin, but because of the difficulty of separating these compounds some indirect proof was necessary. Both hydro- and isohydrobenzoin are oxidized to benzil in quantitative yield when heated with nitric acid. Accordingly, 4 g. of the mixture, m. p. 98–110°, was oxidized with 25 cc. of nitric acid, d. 1.40, on the steam-bath. The heating was continued until the fumes no longer came off—about 90 minutes. The solution was poured into an equal volume of cold water. A yellow solid separated; weight, 3.7 g.; m. p., 64–75°. Recrystallization from alcohol gave 3.1 g. of a yellow solid melting at 90–92°. A mixed melting point showed this to be benzil.

As a further check, the original solid was analyzed for carbon and hydrogen. The sample used melted at 99–111°.

*Anal.* Calcd. for  $C_{14}H_{14}O_2$ : C, 78.43; H, 6.58. Found: C, 78.30; H, 6.55.

**Reduction of Acrolein.**—Seventy-five g. of crystalline vanadous sulfate ( $VSO_4 \cdot 7H_2O$ ) (prepared by the electrolytic reduction of vanadyl sulfate) was dissolved in 300 cc. of water in an atmosphere of carbon dioxide and 20 g. of acrolein added to the brown solution. After one hour the solution was extracted ten times with ether. On distillation, 5 g. (25%) of unchanged acrolein was recovered and the residue on distillation at 20 mm. yielded 6 g. of divinylglycol, b. p. 102–108° (30%), and 7 g. of a thick, yellow oil boiling above 120° (20 mm.) from which no definite product was isolated. The divinylglycol was identified by its boiling point and the formation of the tetrabromide, m. p. 172–173°, by the action of bromine on a cold chloroform solution. When a purple solution of vanadous sulfate containing an excess of sulfuric acid and zinc sulfate (prepared by the reduction of vanadium pentoxide with amalgamated zinc) was employed instead of the neutral brown solution, the yield of divinylglycol was only 9%. In addition, an oil insoluble in water and boiling at 160–167° was obtained. It was unsaturated as shown by its reaction with bromine, but no crystalline dibromide could be obtained. It did not react with sodium bisulfite solution or semicarbazide. On redistillation it was separated into the following fractions; b. p. 164–166°,  $n_D^{23}$  0.14432; b. p. 166–167°,  $n_D^{23}$  0.14435; 167–168°,  $n_D^{23}$  0.14438.

*Anal.* (166–167° fraction). Calcd. for  $C_{12}H_{18}O_2$ : C, 68.5; H, 8.6. Found: C, 69.2; H, 8.8.

Its molecular weight and structure have not yet been determined. By allowing divinylglycol to stand for 24 hours in 2 *N* sulfuric acid it yielded an oil insoluble in water, but on distillation of this and the ether extracts only unchanged glycol and high-boiling tarry material were found.

A careful search for monomolecular reduction products was made in the low-boiling distillates from the ether extract. No material boiling between 90° and 100° was obtained (allyl alcohol, b. p. 96°; propyl alcohol, b. p. 97°). The recovered acrolein was tested for *n*-propyl aldehyde by treating 1 cc. with phenylhydrazine and then with zinc chloride<sup>18</sup> at 180°. A very few crystals with a faint odor of skatole and giving a faint

<sup>18</sup> Fischer, *Ber.*, 22, 104 (1889). Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, 1916, vol. 2, p. 177.

sodium nitroprusside test were obtained. A blank test showed that the original acrolein was entirely free from propyl aldehyde and a test with acrolein containing 20% of propyl aldehyde gave a considerable deposit of skatole crystals.

**Reduction of Crotonaldehyde.**—One hundred g. of crotonaldehyde was run into a well-stirred solution of vanadous sulfate in an atmosphere of carbon dioxide. (The vanadous solution was prepared by the reduction of 190 g. of vanadium pentoxide by amalgamated zinc in 2 liters of water and 400 cc. of concd. sulfuric acid.) After one hour the solution, on which a brown oil floated, was extracted five times with 600 cc. of ether. On distillation, unchanged crotonaldehyde and 65 g. of a light yellow, higher-boiling oil were obtained. This on distillation at 15 mm. yielded: (a) 7.5 g. of oil with an odor of parsley boiling below 100° (15 mm.); (b) 26 g. of yellow oil, b. p. 110–130° (15 mm.); (c) 14 g., b. p. 140–165° (15 mm.); 7.5 g. of black tar as a residue. Fraction b on redistillation yielded 18 g. (18%) of dipropionylglycol which was identified as the tetrabromide (m. p., 120°). Fraction a on redistillation gave 6 g. of colorless oil, b. p. 85–100° (12 mm.),  $n_D^{26}$  0.14608, combined with bromine; it was not further investigated. From Fraction c by redistillation was obtained an oil, b. p. 140–165° (6 mm.);  $d_{20}^{20}$ , 0.9916;  $n_D^{26}$ , 0.14903. It was evidently a mixture of two or more products. A somewhat similar oil was obtained by shaking dipropionylglycol with 2 *N* sulfuric acid, distilling with steam and extracting the residue with ether. On distilling the ether solution a product, b. p. 130–170° (10 mm.),  $d_{20}^{20}$  0.9996,  $n_D^{26}$  0.14969, was obtained. The constants for this mixture are not identical with those of Fraction c given above, but suggest that both mixtures may have contained one or more substances in common. The distillate from the steam distillation contained an oil, b. p. 85–100° (10 mm.), which resembled in odor that obtained from Fraction a above. The results indicate (but do not prove) that the by-products in the crotonaldehyde reduction are secondary products formed from the dipropionylglycol by the action of the acid.

The low-boiling distillates from the ether extract of the reduction process were examined for monomolecular products. Careful fractionation showed that no material boiling at 110–120° (700 mm.) was present; the presence of butyl or croton alcohol was thus excluded. Butyl aldehyde boils at 77°, crotonaldehyde at 104°; the bulk of the recovered aldehyde boiled at 98–106°, but 4 g. was obtained, b. p. 82–81°. These were tested for butyl aldehyde by conversion into the semicarbazone. Half a gram of this 72–81° fraction yielded 0.5 g. of carbazone, m. p. 195°, while 0.5 g. of pure crotonaldehyde under similar conditions yielded 0.8 g. of carbazone, m. p. 195°. A sample of crotonaldehyde containing 30% of butyl aldehyde yielded a carbazone, m. p. 95–150°. The amount of butyl aldehyde (if any) in the 72–81° fraction must, therefore, have been very small and the total yield less than 1 g. (1%).

**Cinnamic Aldehyde.**—Cinnamic aldehyde (100 g.) was added during the course of 30 minutes to a well-stirred solution of vanadous sulfate in an atmosphere of carbon dioxide. (The vanadous sulfate solution was prepared by the reduction of 100 g. of vanadium pentoxide in 1 liter of water and 300 cc. of concd. sulfuric acid by amalgamated zinc.) At the end, 50 cc. of 95% alcohol was added and the stirring continued for one hour. The mixture was extracted with ether six times and the ether distilled. The residue was submitted to steam distillation and the distillate collected in fractions. A sample of the organic layer in each fraction was converted into the semicarbazone. In every case the melting point and yield of the semicarbazone corresponded to those obtained in a parallel experiment with pure cinnamic aldehyde. It was, therefore, concluded that no appreciable quantities of monomolecular reduction products (cinnamic alcohol, hydrocinnamic alcohol or aldehyde) were present. The residue in the distilling flask was dissolved in ether and extracted with sodium bisulfite to remove the remaining traces of unchanged aldehyde. In all 50 g. of unchanged cinnamic aldehyde was re-

covered of which a sample yielded the same amount of pure semicarbazone as that given by the corresponding amount of pure aldehyde. From the thick, oily residue after distilling the ether, 7 g. of diphenylvinylglycol, m. p. 154°, was obtained. It was further identified by conversion to the diacetate, m. p. 119°. No further crystalline product could be obtained from the thick, oily residue, and efforts to obtain a crystalline diacetate or dibenzoate were fruitless. The oil combined with somewhat less than two molecular equivalents of bromine, but no crystalline bromide could be obtained.

### Summary

1. Chromous chloride in aqueous or alcoholic solution has been found to be without effect at 25° on representative aliphatic aldehydes and ketones, aromatic ketones, saturated and unsaturated acids and esters, alcohols, ethylene or diphenylbutadiene.

2. Typical aromatic aldehydes,  $\alpha,\beta$  unsaturated aldehydes, benzalacetophenone and certain other  $\alpha,\beta$  unsaturated ketones are reduced by chromous chloride and vanadous chloride with the formation of dimolecular products. Mesityl oxide is not reduced. The amount of monomolecular reduction, if any, must be very small.

3. It seems probable that the dimolecular reduction process proceeds through an addition product of the carbonyl compound and the inorganic acid present and is analogous to the reduction of the halochromic salts of aryl carbinols.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

## SYMMETRICAL DI-METHYLPHENYLMETHYL-HYDRAZINE AND RELATED COMPOUNDS<sup>1</sup>

BY W. A. SCHULZE AND H. L. LOCHTE

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Previous papers<sup>2</sup> have shown that aliphatic hydrazines which are not readily prepared by older methods may be obtained by catalytic reduction of the corresponding ketazines. The reduction of acetophenone ketazine has now been accomplished and various derivatives of the reduction product have been prepared.

Acetophenone ketazine was first prepared by Curtius and Thun<sup>3</sup> by the usual method. The yield, even after the reaction mixture had been heated under a reflux condenser for 12 hours, was evidently not good, as they reported the formation of a yellow oil which later was identified<sup>4</sup> as

<sup>1</sup> Constructed from a thesis submitted by W. A. Schulze in partial fulfillment of the requirements for the degree of Master of Arts at the University of Texas.

<sup>2</sup> (a) Lochte, Bailey and Noyes, *THIS JOURNAL*, **44**, 2556 (1922). (b) Harkins and Lochte, *ibid.*, **46**, 450 (1924).

<sup>3</sup> Curtius and Thun, *J. prakt. Chem.*, [2] **44**, 167 (1891).

<sup>4</sup> Curtius and Pflug, *ibid.*, [2] **44**, 540 (1891).