

metric method under the influence of a number of acids and bases of various electric charge types. The results of the experiments have given strong support to the theory presented.

3. The catalytic effect of acid and basic molecules on the mutarotation of glucose increases with their strength as acids and bases. There seems to be a simple relationship between catalytic efficiency and strength, shown by the fact that a logarithmic plot of the basic catalytic constant against the basic strength constant, covering the range of 10^{18} in the latter, comes out approximately as a straight line with slope about 0.4.

4. The laws of mutarotation are in marked conformity with the laws previously found for the decomposition of nitramide.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

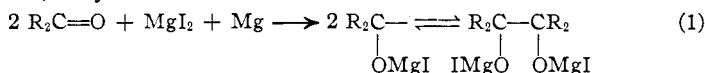
THE REDUCTION OF BENZIL BY THE BINARY SYSTEM, MAGNESIUM + MAGNESIUM IODIDE (OR BROMIDE)

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Recently we described the reducing action of a mixture of magnesium iodide (or bromide) and magnesium on aromatic ketones.¹ This class of ketones was found to give pinacolates through the intermediate formation of free radicals, ketyls

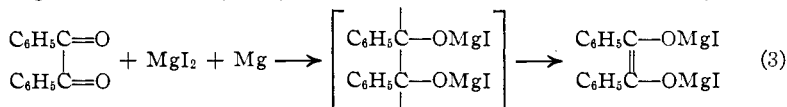


According to our hypothesis, the active reducing agent was magnesium subiodide, generated by the interaction of the metal and halide



and present as such only in minute quantities at any one moment. The reaction has now been extended to the diketone, benzil.

Benzil with its two carbonyl groups reacts with the binary system fundamentally in much the same fashion as do the aromatic ketones, except that here the newly created carbon-carbon bond remains within the original molecule, giving rise, therefore, to an unsaturated glycolate.

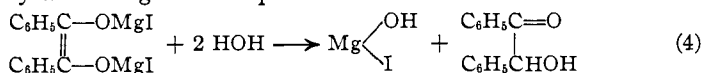


The reaction proceeds *quantitatively* according to the above equation. In the process of reduction the solution displays a series of deep colors, green, brown, red and finally yellow. The halomagnesium glycolate

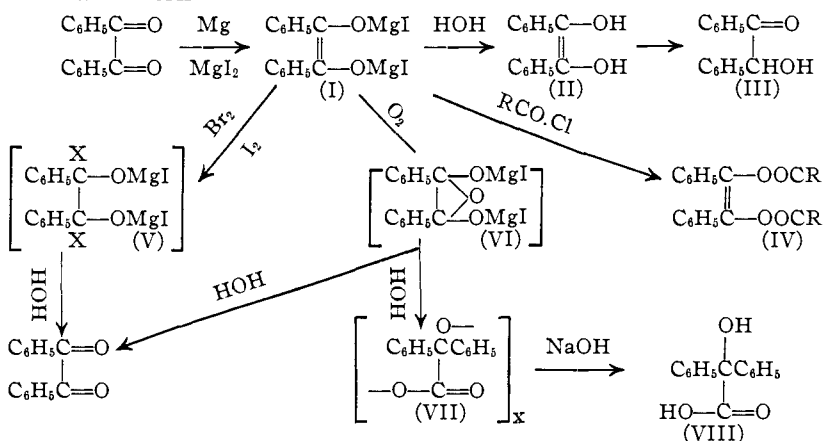
¹ (a) Gomberg and Bachmann, *THIS JOURNAL*, **49**, 236 (1927); (b) Gomberg, *Chem. Reviews*, **2**, 309 (1925).

(I) was isolated in solid, crystalline state; it was found to be colorless and to have the composition indicated by the formula.

On hydrolysis this glycolate gives the unsaturated glycol, stilbene-diol, $C_6H_5C(OH)=(HO)CC_6H_5$ (II), which tautomerizes rapidly to the stable form, benzoin (III). Titration of the magnesium hydroxide and estimation of the benzoin produced showed that the hydrolysis proceeds quantitatively according to the equation:



Like the benzil dipotassium compound, $(C_6H_5COK=)_2$, of Staudinger and Binkert,² and the benzil disodium derivative of Nef,³ the unsaturated halomagnesium glycolate reacts with benzoyl chloride and gives α,β -dihydroxystilbene dibenzoate (IV); with acetyl chloride the corresponding diacetate is formed.



Benzyl chloride and methyl iodide were used in the attempt to make ethers, but not much reaction took place with these reagents. With triphenylchloromethane, however, a decided reaction occurred with the formation of benzil and triphenylmethyl.

Iodine and bromine are absorbed mole for mole by the halomagnesium glycolate, the resulting mixtures on hydrolysis giving practically quantitative yields of benzil. The reaction is best formulated as giving the hypothetical compound (V), although it is equally probable that the halogen may detach the MgI without previously adding itself to the glycolate. The reaction with bromine requires but a few minutes; that with iodine is slower.

Considerable heat is generated on exposing the solid glycolate to the air. A solution of the compound, which is transparent and light yellow in

² Staudinger and Binkert, *Helv. Chim. Acta*, 5, 703 (1922).

³ Nef, *Ann.*, 308, 287 (1899).

color, instantly becomes opaque, dark brown in color through the action of even a minute amount of oxygen. The total amount of oxygen that can be taken up corresponds to one atom of oxygen for one mole of glycolate. The primary products of oxidation are probably in the form of an oxide (VI). Addition of water yields benzil and a compound that gives benzilic acid on hydrolysis and may be considered as a polymer of the anhydride of this acid (VII); frequently some benzoic acid is also produced. Because of the extreme sensitivity of the glycolates to oxygen, great care had to be exercised throughout this work to prevent undue exposure to air.

Not only the binary system magnesium-magnesium halide can accomplish the reduction of benzil, but other systems as well can bring about the same reaction with varying degrees of rapidity, even when the metal element is not the same as the metal in the halide.

In view of the remarkable reactivity of the glycolate, is it not possible that we have here a partial opening of the double bond to a single bond, giving rise to two reactive trivalent carbon atoms in the same molecule? Similar explanations have been advanced in order to account for the unusual reactivity of certain compounds.⁴

Experimental

Reduction of Benzil.—(a) By $MgI_2 + Mg$. A solution of magnesium iodide was prepared from 5.2 g. (0.04 atom) of iodine and excess of powdered magnesium in a mixture of 20 cc. of anhydrous ether and 40 cc. of dry benzene. The colorless solution was filtered into a 70cc. test-tube and 4.20 g. (0.02 mole) of benzil was added; a reddish colored solution resulted at this point, due in part to liberation of iodine (see discussion, p. 2591). A weighed rod of magnesium (8.9900 g.) was inserted and the tube carefully stoppered with a cork. Almost immediately red streamers began to flow from the rod and the solution soon possessed a deep reddish-brown color. After a time the color changed to an opaque greenish-black. In the course of 18 hours the solution became lighter in appearance, shifting to a reddish-brown, then to red and finally to a light yellow color. At the end of the reaction a perfectly clear, transparent solution remained. The rod was removed, and it now weighed 8.5020 g., which represents a loss of 0.4880 g. The theoretical value (Equation 3) is 0.4864 g. (0.02 atom). Dozens of such estimations gave values differing by only a few milligrams from the theoretical.

By using an excess of magnesium turnings complete reduction was effected in one hour; when magnesium powder was employed 10–20 minutes were sufficient to carry 4.20 g. of benzil through the color changes just described. When exactly 0.4864 g. of magnesium turnings was added to 4.20 g. of benzil, the latter was completely reduced and no trace of metal remained at the end of the reaction. The advantage of using a rod is obvious; it can be readily withdrawn from the solution at any time and weighed, thus allowing the reaction to be studied on a strictly quantitative basis.

(b) By $MgBr_2 + Mg$. The procedure here was identical with that above except for the preparation of the halide. The synthesis of magnesium bromide from the elements is not feasible; accordingly it was prepared⁵ from mercuric bromide and mag-

⁴ (a) Gomberg and Bachmann, *THIS JOURNAL*, 49, 247 (1927); (b) Ingold and Marshall, *J. Chem. Soc.*, 129, 3080 (1926); (c) Zelinsky and Kozeschkow, *Ber.*, 60, 1108 (1927); (d) Scholl, *Ber.*, 60, 1236 (1927).

⁵ Ref. 1 a, p. 245.

nesium. Five g. of dry mercuric bromide is placed in a flask with 25 cc. of ether and 10 cc. of benzene, a reflux condenser being provided. One and one-half g. of magnesium powder is now added, followed by 30 cc. of benzene and then the mixture is boiled until reaction is complete. After the mixture has stood for a time the supernatant liquid is decanted through a hardened filter paper; there is thus obtained a pure, colorless solution of anhydrous magnesium bromide. As a rule the mixture was filtered into a narrow graduated cylinder, 1 cc. of the solution removed, decomposed with water, and the concentration of $MgBr_2$ determined by titration with silver nitrate solution. The exact volume of the salt solution requisite for the experiment could now be calculated. The above ether-benzene mixture is capable of dissolving magnesium bromide to the extent of 0.75–0.80 *N*.

For most experiments we used solutions of the glycolate, prepared as above, since the isolation of the solid glycolate itself is accompanied by loss of material. Usually the iodide was used because of the ease of its preparation. For some purposes, as in the study of the color phenomena, the bromide proved more suitable; this was also the case when it was desired to isolate the reaction products in the solid state, the bromide being less soluble than the iodide.

Isolation and Analysis of the Bromomagnesium Glycolate.—This compound is quite soluble when the proportion of benzene to ether is large. In ether alone it is not very soluble, but the reduction of benzil in this solvent is ever so much slower, due to the formation of some magnesium etherate compound in the form of an insoluble oil. Excellent reduction and precipitation occurs in a mixture of solvents consisting of 1 part of benzene to 3 parts of ether. Furthermore, this mixture dissolves magnesium bromide more readily than one richer in benzene.

A solution of magnesium bromide was prepared from 20 g. of mercuric bromide and magnesium in 54 cc. of ether and 18 cc. of benzene. Eight and four-tenths g. of benzil was added and a rod of magnesium inserted. In ten minutes the solution became green, and this color persisted for two days, when the solution became brown. Several days later the reduction was complete; however, shaking was continued for several weeks. During this time a large amount of white, granular glycolate precipitated out. The crystals were filtered from the solution and washed several times with ether-benzene mixture (3:1) and finally with ether alone. After the free solvent had been removed, the crystals weighed 9.82 g. All operations were carried out in an atmosphere of dry nitrogen, for the glycolate is extremely sensitive to oxygen and moisture.

Weighed samples of the solid were decomposed with water; the magnesium hydroxide thus produced was determined by titration with acid; the bromine by titration with silver nitrate; and the benzoïn, containing a small amount of oxidation products, was isolated, dried and weighed. On a separate sample the total magnesium was determined as MgO by ignition with nitric acid. The solvent of crystallization was obtained by difference, and it was found that the glycolate crystallized with two molecules of ether. From the results of analysis, the percentages of the constituents were calculated on a solvent-free basis. The results given below were obtained on samples each of which came from a different reduction experiment.

Anal. Subs., 4.982, 1.197, 3.750. Calcd. for $(C_6H_5COMgBr)_2$: benzoïn, 50.3; Mg, 11.6; Br, 38.3. Found: benzoïn, 49.9, 50.6, 49.1; Mg, 12.6, 11.6, 11.7; Br, 38.3, 37.8, 39.2.

Reduction of Benzil to Glycolate is Quantitative.—Since the glycolate is somewhat soluble it cannot be isolated in quantitative yields from the reduction mixture. We

have proved, however, that the reduction of benzil to the glycolate is, nevertheless, quantitative, by hydrolyzing the reduction mixture itself without previous isolation of the solid glycolate. Repeated runs on 4.20g. samples of benzil gave with water yields of benzoin corresponding to 92-95%. Finally, an experiment was carried out, with rigorous exclusion of air throughout, in which one-tenth of a mole of benzil was reduced, the solution hydrolyzed and the amounts of the components carefully determined.

The colorless solution of magnesium iodide from 28 g. of iodine and 5 g. of magnesium in 50 cc. of ether and 200 cc. of benzene was filtered into a 300cc. Drechsel bottle filled with nitrogen and containing 21.00 g. of benzil. A dark red solution resulted. A weighed rod of magnesium was inserted and the bottle was tightly stoppered by means of a cork. Reaction began immediately with the characteristic production of successive color effects. At the end of 45 hours the solution was light yellow; no precipitate of any kind was present. The magnesium rod was withdrawn, washed, dried and weighed. Loss in weight, 2.435 g.; calculated, 2.431 g.

The clear ether-benzene solution was poured into water which had been freed from air by boiling. Dilute sulfuric acid was used to dissolve the copious precipitate of magnesium hydroxide that had been produced. One and one-half liters of benzene was required to dissolve the benzoin that had crystallized out. The solution was filtered from the small amount of insoluble white substance, which consisted of oxidized glycolate with some magnesium hydroxide adsorbed or occluded. This product weighed 0.25 g., and gave on hydrolysis with sodium hydroxide 0.17 g. of benzilic acid. The main solution was extracted with dilute sodium carbonate and this alkaline solution gave an additional 0.08 g. of benzilic acid.

After the treatment with sodium carbonate, the ether-benzene solution was dried over calcium chloride and the solvent removed by distillation. The white, solid residue, consisting of benzoin and a small amount of benzil, was digested with 70 cc. of cold anhydrous ether in order to remove the benzil, the mixture was filtered, and the undissolved benzoin was washed with ether, in which it is only slightly soluble. The ethereal extract was evaporated to dryness and the light yellow solid was extracted in a Soxhlet extractor with 30-40° petroleum ether. The benzoin is almost completely insoluble in this solvent while the benzil is readily soluble. The separation is as nearly quantitative as can be desired. In the extraction thimble was left 0.32 g. of benzoin; from the petroleum ether extract was obtained 0.42 g. of benzil. In spite of all precautions taken, there still resulted some oxidation of the glycolate to benzil and polymerized benzilic acid. The results may be summarized as follows: benzoin, 20.48 g. (96.6%); benzil, 0.42 g. (2.0%); polymer + benzilic acid, 0.25 g. (1.2%).

We feel justified, therefore, in stating that the reduction of benzil to glycolate is quantitative. In using for our many experiments the reduction solution of benzil without previous isolation of the glycolate, we have thus taken for granted that the amount of glycolate in the solution corresponds exactly to the amount of benzil taken.

The reaction of benzil with magnesium may proceed to completion, although more slowly, in the presence of even small amounts of magnesium halide. For example, yields of benzoin amounting to 78-94% were obtained, though the amount of magnesium halide was only 1-25% of a mole. In all cases the theoretical amount of magnesium was dissolved. As happens with the pinacolates,⁶ the metal halide is continuously split off from the halomagnesium glycolate and is thus made available for

⁶ Ref. 1, p. 243.

further reaction. The magnesium glycolate, $C_6H_5C=CC_6H_5$, is less

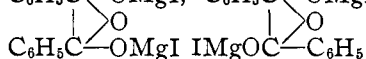


soluble than its precursor and so precipitates out as a colorless solid during the reduction.

Reaction with Oxygen.—The amount of oxygen that can be taken up by the glycolate was measured by means of the absorption apparatus usually employed for similar purposes in the study of free radicals. In the gas buret was placed the same mixture of solvents as was used for the solution of the glycolate, and the bottle was shaken by mechanical means. A solution of the glycolate from 2.10 g. of benzil was connected to the absorption apparatus. Soon the solution became dark brown as the oxygen was taken up. The total volume absorbed was 97 cc. (corr.); calculated for one atom of oxygen to one mole of glycolate, 112 cc. Absorption was rapid at the beginning, gradually becoming slower. Hydrolysis showed the presence of 5% of unoxidized glycolate, 40% of benzil, 40% of benzoic acid polymer and 13% of benzoic acid.

A number of experiments were performed in which the amount of oxygen was not measured, dry air or oxygen being passed through the solution of the glycolate until oxidation was complete. Both the bromomagnesium and the iodomagnesium salts of the stilbene-diol yield the same products on oxidation, benzil (43–73%), benzoic acid, free and as polymer, (17–32%) and benzoic acid (5–16%). The bromomagnesium glycolate becomes colorless on oxidation while the iodomagnesium compound liberates a large amount of iodine. Staudinger and Binkert² obtained only benzoic and benzoic acids and no benzil on oxidation of the potassium salt of the stilbenediol.

Although oxidation of the glycolate and subsequent hydrolysis of the product results in the production of benzil and polymerized benzoic acid, yet very little, if any, of these are present as such in the solution before water is added. Repeated experiments have shown that colorless solutions of completely oxidized bromomagnesium glycolate, when subjected anew to re-reduction with magnesium, display no characteristic color phenomena and no loss of metal occurs. The benzil and the polymer prior to hydrolysis must, therefore, exist in the form of some non-reducible magnesium compound such as the oxide (VI). Whether on oxidation only a single compound (VI) is formed, which on hydrolysis gives rise to the two substances, benzil and polymer, or whether these two substances come from two distinct oxidation products cannot be decided at this time. It is not unlikely that two stereo-isomeric oxides are produced, *cis* and *trans*, $C_6H_5C-OMgI$, $C_6H_5C-OMgI$, one of which



on hydrolysis gives benzil; the other, either before or after hydrolysis, under-

goes rearrangement to the benzoic acid derivative. Other derivatives of the glycol are known to exist in two forms.²

Color Effects during Reduction.—Although the halomagnesium glycolates are colorless in the solid state and are only light yellow in solution, yet when mixed with benzil, especially in equivalent amounts, deep brown solutions are produced. The same colors persist in the solution during reduction of benzil to the glycolate as long as any unreduced benzil is present. They are also formed when the colorless glycolate becomes partially oxidized by air. Under certain conditions the initial color produced on reduction of benzil is brilliant emerald-green. The bromide forms this most readily, solvent and concentration being important factors upon which the formation of the green color depends. Ether was found to favor the formation of green, benzene that of red. With magnesium bromide the initial color is green even with benzene-ether in the ratio 1:1; with magnesium iodide the red color usually appeared, but by using almost entirely ether, green also could be obtained. Moreover, dilution of a green mixture gave a reddish-brown color.

Characteristic color effects have been obtained also in the case of the sodium and potassium derivatives of benzil. Schlenk and Thal⁷ consider the blue compound which they obtained to be a substance containing

a trivalent carbon atom, $C_6H_5C(OK)-COC_6H_5$; Nef and Staudinger and Binkert are of the opinion that this compound is the quinhydrone, $[C_6H_5C(OK)=(KO)CC_6H_5][C_6H_5CO-COC_6H_5]$. Whether in our case

the green color represents a free radical, $RC(OMgX)-COR$, or whether both the green and the brown are two distinct quinhydrone compounds, each requiring certain specific conditions for existence, is left undecided.

Reaction with Benzoyl Chloride and with Acetyl Chloride.—The clear yellow solution of the glycolate prepared from 4.20 g. of benzil was treated with a solution of 6 g. of benzoyl chloride in 15 cc. of ether and 30 cc. of benzene. In three minutes a white precipitate of magnesium salt began to settle out. After the mixture had stood for 15 hours water was added. The crude product obtained from the organic solvents was recrystallized by dissolving it in a small amount of hot benzene and adding petroleum ether. The dibenzoate of the stilbene-diol was obtained in the form of large, glistening crystals, m. p. 157–158°; reported in the literature, 159°; yield, over 75% of that possible. In like manner the corresponding diacetate was prepared; m. p. 116–117°. Nef and Staudinger and Binkert give 118–119°.

Reaction with Alkyl Halides.—A warm solution of triphenylchloromethane in 20 cc. of benzene was added to a solution of iodomagnesium glycolate from 3.00 g. of benzil, care being taken to prevent access of air. As the two solutions were mixed a deep green color was produced and a white precipitate of magnesium salt appeared. On shaking the mixture, the green color gave way to a bright orange and the mixture became very thick with the solid. After being warmed for one hour and standing at room temperature for several hours, the product was decomposed with water; there was no precipitation

⁷ Schlenk and Thal, *Ber.*, **46**, 2850 (1913).

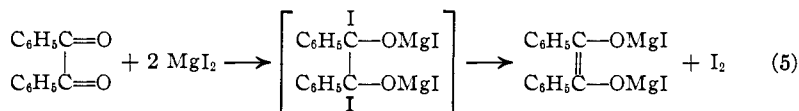
of magnesium hydroxide, showing that reaction was complete. The benzene-ether solution was filtered from a few large, brilliant yellow crystals (triphenylmethyl ether of the unsaturated glycol ?); m. p. 180–190°. From the solution was isolated 2 g. of benzil and the following oxidation and reduction products of triphenylmethyl: 1.5 g. of triphenylcarbinol, 1 g. of triphenylmethane, 0.25 g. of triphenylmethylperoxide. With benzyl chloride and with methyl iodide the glycolate showed no reaction.

Reaction with Bromine and with Iodine.—A solution of 3.43 g. of bromine in 50 cc. of carbon tetrachloride was used for titration of the glycolate from 4.20 g. of benzil and all operations were carried out in an atmosphere of nitrogen. The bromine was absorbed as fast as it was added. A few drops were sufficient to change the yellow color of the bromomagnesium glycolate solution to a dark brown color; further addition produced an opaque brownish-black mixture, and as more bromine was dropped in the solution became lighter in color, going to a transparent red, then to orange and finally to the yellow of benzil solution, which was taken as the end-point. Calcd. for 1 mole of bromine to 1 mole of glycolate: 3.15 g. Found: 3.15 g. Decomposition with water gave 4.00 g. of benzil (95%).

With iodine, instead of titration, the calculated amount of solid iodine was introduced at one time. A considerable amount of heat was generated in the reaction that followed and the solution became opaque brownish-red in color. After half an hour the mixture was translucent, but even after ten days some iodine was still present. Addition of water, followed by the usual separations, gave 94% of the calculated amount of benzil, the other products being benzoic acid, 3%, and benzoin, 1%.

Reaction of Benzil with Magnesium Bromide and with Magnesium Iodide.—Magnesium bromide and benzil form a complex without perceptible change in the yellow color of the solution. By keeping a mixture of 5.25 g. of benzil and 4.5 g. of magnesium bromide in 25 cc. of ether and 35 cc. of benzene in a cool place for two weeks, a large amount of nearly colorless crystals was obtained. The complex was found to have the composition $(C_6H_5CO-COC_6H_5) \cdot MgBr_2 \cdot (C_2H_5)_2O$. It is readily decomposed by water into its constituents.

The addition of benzil to a solution of magnesium iodide gives rise to a deep red color, occasioned in part by liberation of iodine. A mixture of 4.20 g. of benzil and 5.5 g. of magnesium iodide in 60 cc. of benzene-ether was kept in a dark place for 12 hours. The solution was then poured into water containing a small amount of acid. By titration with sodium thiosulfate 0.32 g. of free iodine was found to be present and there was formed a corresponding amount of magnesium hydroxide. Although the most careful search failed to reveal the least amount of benzoin, we have none the less tentatively assumed the existence of an equilibrium reaction



If oxygen be passed through such a mixture, the glycolate, if actually present, would be fixed as the oxide (VI), thus driving the reaction to the right. Accordingly, dry air was passed through a warm solution of 2.0 g. of benzil and 7.5 g. of magnesium iodide in ether-benzene for two hours. The solution was then hydrolyzed; there were obtained benzil and benzoic acid polymer, 50% of each, and 3.17 g. of iodine was found to be present.

Yet another method suggested itself whereby the assumed reaction could be driven to the right, namely, by removing the iodine by means of some metal other than magnesium. We have found that the addition of molecular silver, of mercury or of zinc actually accomplishes this result and that halomagnesium glycolate is formed in con-

siderable amounts. On hydrolysis yields of benzoin were obtained that corresponded to 55-79% of that possible.

Magnesium bromide, unlike the iodide, gives with benzil no detectable amount of free halogen. Nevertheless, when silver, mercury or zinc is added reaction sets in, in some cases very slowly, and there is produced bromomagnesium glycolate. Hydrolysis resulted in benzoin being formed to the extent of 50-60%.

Benzil with Other Binary Systems.—The binary system Be-BeI₂ with benzil after five days of shaking gave a 95% yield of benzoin on addition of water; the system, Zn-ZnI₂, gave a 71% yield after 22 days. The amount of benzoin indicates the extent of reduction.

Reduction of Benzil by Magnesium Amalgam.—Magnesium alone has no effect on benzil, but in the presence of mercury, which soon coats the magnesium with amalgam, reaction takes place with the production of the usual dark, reddish-brown color. On hydrolysis a 72% yield of benzoin was obtained. Likewise, amalgam prepared by heating together magnesium and mercury was able to reduce benzil.

Mechanism of the Reaction.—The reaction between magnesium, magnesium halide and ketone has been interpreted by us not as a trimolecular reaction but as one consisting of two bimolecular reactions: (a) a subhalide of magnesium, MgX, is formed; (b) the subhalide adds itself to the oxygen of the carbonyl group. This interpretation we now find fully applicable to the diketone, benzil.

Since benzil, when acted upon by MgX₂ in the presence of silver or mercury, gives the unsaturated halomagnesium glycolate, other interpretations are possible. An unstable addition product may be formed from which the halogen, linked to the carbon atom, is then taken up by the metal directly or through its previous rejection as free halogen (Equation 5).

Considerably more experimental evidence is essential before a final explanation, or explanations, can be advanced as to the mechanism of the reduction accomplished by the various binary systems.

Summary

Benzil in ether-benzene is reduced by the binary systems, Mg-MgI₂ and Mg-MgBr₂, quantitatively to the halomagnesium salt of stilbene-diol, $C_6H_5C(OMgX)= (XMgO)CC_6H_5$.

These unsaturated glycolates were found to be extremely reactive with various reagents; with water benzoin is produced; with acid chlorides esters result; bromine and iodine yield benzil; with oxygen two products are formed, benzil and a polymer of the anhydride of benzilic acid.

Other binary systems were found to reduce benzil in a similar manner. The possible mechanism of the reduction has been discussed.

It may be added that considerable data have been accumulated on the behavior of aliphatic-aromatic ketones, aromatic aldehydes and esters toward the binary systems. The reactions seem to be more complex, though in general of the same nature as described for the ketones.