

water. Method of preparation and analytical results show this substance to be ditolyl-tetrabromo-phthalide.

Analysis. Calc.: Br, 50.83. Found: 51.08.

Tetra-iodo-phthalic Anhydride with Aluminum Chloride and Benzene.—Ten g. of anhydride, 40 cc. of benzene, 4.4 g. of aluminum chloride and 6 cc. of acetic anhydride were taken, the temperature of reaction being about 80°. The phthalide obtained is soluble in benzene, toluene and chloroform, slightly soluble in ether, ligroin and ethyl alcohol, and insoluble in water. When recrystallized from glacial acetic acid it melted at 206°; yield, 61%. It has a very pale yellow color. This compound was shown to be diphenyl-tetra-iodo-phthalide.

Analysis. Calc.: I, 64.33. Found: 64.01.

Tetra-iodo-phthalic Anhydride with Aluminum Chloride and Toluene.—The reaction was carried out as above at 97–98° with 10 g. of anhydride, 40 cc. of toluene, 4.4 g. of aluminum chloride, and 6 cc. of acetic anhydride. The product was treated with small quantities of cold acetone to remove the tar formed during the reaction. The residue was recrystallized from glacial acetic acid and melted at 213–214°; yield, 42%. It is soluble in benzene and chloroform, and slightly soluble in ethyl and methyl alcohols ether and ligroin. Our purest product had a pale yellow color. The synthesis and analysis show this substance to be ditolyl-tetra-iodo-phthalide.

Analysis. Calc.: I, 62.1. Found: 62.5.

Summary.

1. The method used by Rubidge and Qua for the preparation of diphenyl phthalide was found to give good results in the preparation of the diphenyl and ditolyl tetrahalogen phthalides.
2. Four new substituted phthalides have been prepared and their properties described: diphenyl-tetrabromo-phthalide, m. p. 202°; ditolyl-tetrabromo-phthalide, m. p. 196–197°; diphenyl-tetra-iodo-phthalide, m. p. 206°; ditolyl-tetra-iodo-phthalide, m. p. 213–214°.

TORONTO, ONTARIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE REARRANGEMENT OF BENZIL TO BENZILIC ACID.

By ARTHUR LACHMAN.

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The mechanism whereby benzil, under the influence of alkalis, is converted into benzilic acid has long been a matter of speculation. Four different hypotheses have occupied the attention of recent investigators. Nef¹ assumed an addition of water to benzil, followed by dissociation into benzophenone and "dioxymethylene;" the latter substance, after changing over into formic acid, was then supposed to condense with the former by carbonyl condensation, thus yielding benzilic acid. Schroeter² postulated the intermediate formation of diphenylketene. This view, however, has been tested experimentally by Nicolet and Pelc,³ and found untenable. Tiffeneau, recognizing the analogy between the benzil rearrangement

¹ Nef, *Ann.*, **298**, 372 (1897).

² Schroeter, *Ber.*, **42**, 2336 (1909).

³ Nicolet and Pelc, *THIS JOURNAL*, **43**, 935 (1921).

and that of pinacol into pinacolone, has adapted his theory of the latter process⁴ to the somewhat different conditions applying in the case of benzil. Michael,⁵ in a purely critical consideration of these explanations has found them all unsatisfactory; according to him, the rearrangement of benzil is caused by "the great positive energy of the alkali" employed as reagent.

An experimental study of this puzzling behavior of benzil has brought facts to light which definitely rule out the hypotheses of Nef, Tiffeneau and Michael. This work was suggested by the recently completed investigation of dihydroxy-tartaric acid⁶ during which the striking resemblance of this acid to benzil was noted. Dihydroxy-tartaric acid, warmed with alkali, rearranges to give tartronic acid; this process is quite analogous to the benzil transformation. Dihydroxy-tartaric acid, whose carboxyl groups hold water and are therefore C(OH)₂ groups, is able to undergo rearrangement simply through the action of heat.⁷ Is it not possible that benzil, given sufficient time and temperature increase, might add water and produce benzilic acid?

The Action of Water on Benzil.

Michael and Tiffeneau base their theoretical views on the preliminary addition of alkali to the benzil molecule. It is strange that they both overlooked the significance of an observation recorded many years ago by Klinger.⁸ Klinger exposed a solution of benzil in moist ether to the action of sunlight; among the reaction products he found benzilic acid.

It was therefore extremely probable that water alone would convert benzil into benzilic acid. The first attempts, however, were not very encouraging. Varying amounts of the two materials were heated in sealed tubes for periods up to 10 hours and to temperatures up to 235°. In all cases, mere traces of benzilic acid were formed, and the benzil was recovered practically completely and with unchanged melting point.⁹

⁴ Tiffeneau, *Rev. gen. sci.*, **18**, 584 (1907).

⁵ Michael, *THIS JOURNAL*, **42**, 812 (1920).

⁶ Lachman, *ibid.*, **43**, 2091 (1921).

⁷ Solutions of the free acid (and its salts) change into tartronic acid even at room temperature; the process is completed within a few days.

⁸ Klinger, *Ber.*, **19**, 1868 (1886). No quantitative data are given; the period of exposure was 4 months. The observation is correct. By means of the colorimetric method described below, it is very easy to follow the progress of this conversion. The ethereal solution is extracted at intervals with small amounts of sodium carbonate solution. Ten g. of benzil, dissolved in 100 cc. of moist ether, gave no test for benzilic acid after 3 days. After 15 days, 0.0015 g. was noted; after 35 days, 0.0020 g. additional was found. The study of this photochemical reaction is being continued.

⁹ Minute amounts of benzilic acid may be estimated with fair accuracy by means of the intense purple color which the substance gives with conc. sulfuric acid. Standards may be made with from 0.0005 to 0.0050 g. dissolved in a few drops of water or alcohol

When the mode of procedure was changed, and benzil was heated under a reflux condenser with large quantities of water, for much longer periods (up to 120 hours), much larger amounts of benzilic acid were obtained. The solubility of benzil in boiling water was found to be 0.33 g. per liter. The solution has a decided yellow color; when it cools, it deposits very slender, and very pale needles. These melt at the same temperature as the original material.

The isolation of benzilic acid from the reaction mixtures was effected as follows. After cooling the material to room temperature, it was made alkaline by the addition of a few cubic centimeters of sodium carbonate solution, and then extracted twice with ether. The alkaline solution was evaporated to about 15 cc., cooled, acidified with hydrochloric acid in slight excess, and extracted with ether. The ether extract was dried at 100° and weighed. Its melting point was then taken. Control tests, each of 1 liter of cold saturated aqueous solution of benzil, gave no benzilic acid whatever when subjected to the process just described.

The first series of measurements gave the following data.

Time Days	Water Cc.	Benzil G.	Benzilic Acid G.	M. p. ° C.
3	1000	10	0.04	140
3	1000	10	0.07	142
5	750	1	0.06	145
3	750	1	0.05	143

The melting points indicate a relatively high degree of purity in the product, and in particular the absence of any considerable proportion of benzoic acid. Pure benzilic acid melts at 149–150°; a mixture with 5% of benzoic acid melts at 142–143°; with 10%, at 134–135°.

These results showed that the active mass, in the conversion of benzil to benzilic acid, is solely the dissolved portion, *i. e.*, 0.33 g. per liter. Based on this amount, the yields of benzilic acid obtained are relatively large.

The method by which these figures were obtained did not lend itself to accurate measurement; but as the data showed that practically no other acid product than benzilic acid was formed, a series of observations was made in which the final acidity was determined. Three flasks containing benzil and water were sealed and kept for 5 days in an electrically heated air-bath. The temperature ranged between 95° and 100°.

The water had previously been boiled to remove carbon dioxide; the and made up to 25 cc. with pure sulfuric acid. If protected from atmospheric moisture these solutions will keep for days. Benzil and benzophenone do not interfere. Benzohydrol gives a brick-red color, but much less intense; it may be removed by ether extraction after rendering the sample alkaline. Phenolphthalein interferes with the benzilic test, and should be employed only as an outside indicator.

flasks were of Pyrex glass, and had been steamed out. At the end of the heating period the flasks were cooled to room temperature, the contents filtered cold, and promptly titrated cold with 0.1 *N* sodium hydroxide solution, with phenolphthalein as an indicator. The following data were secured.

Benzil G.	Water Cc.	NaOH Cc.	Equivalent benzilic acid G.
1.523	500	0.80	0.018
0.884	500	0.65	0.015
0.461	500	0.75	0.017

These figures are somewhat lower than the previous set, despite the longer time period. The temperature was a little lower, however; and the first series may have been slightly influenced by alkali from the glass. Such an influence is excluded here: *free acid only* is recorded.

Action of Very Weak Alkali on Benzil.

Michael's discussion of the benzil rearrangement begins with this statement:¹⁰ "There is no indication of the formation of a hydrated benzil but, even accepting its existence during the reaction, it is certain that alkali would rupture the carbon linkage and form sodium benzoate and benzaldehyde, etc." It has just been shown that water by itself produces little or no benzoic acid. The effect of small amounts of alkali was therefore investigated.

One g. of benzil was boiled with 750 cc. of water as before, with the addition of 5.0 cc. of *N* sodium hydroxide solution. If all the benzil were converted into either benzilic or benzoic acid, 4.4 cc. would be used up. The normality of the alkaline solution at the start was 0.0066. Boiling was continued for 2 days when it was found that 2.5 g. of sodium hydroxide was used up, and 0.55 g. of benzilic acid obtained of m. p. 142°. A duplicate was refluxed for 3 days; 2.8 g. of sodium hydroxide was used up and 0.61 g. of benzilic acid (m. p. 139°) obtained.

The melting points are depressed in part by the phenolphthalein present, and perhaps by other impurities as well: in fact, the crude benzilic acid darkened considerably as it dried before it was weighed, and blackened when it melted; whereas mixtures of pure benzilic and benzoic acids may be re-melted several times without change of color, if not overheated. It is clear, therefore, that the amount of benzoic acid formed during the action of very weak alkali on benzil must be even less than the melting points would indicate, and that 5% is an upper limit.

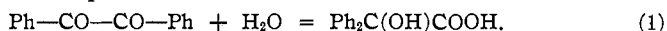
The action of weak alkali on benzil is seen to differ from that of pure water only in the rate at which the rearrangement takes place. The catalytic effect of the alkali, in the concentration employed, is quite moderate; the rate being increased about 20 times. Inasmuch as the hydroxyl-

¹⁰ Ref. 5, p. 812.

ion concentration in the alkali is nearly 10,000 times greater than in the water, the hydroxylion as such is not an essential factor in the transformation. The relative unimportance of this ion is shown also by the final acid reaction when water alone is the reagent.

The views of Tiffeneau and of Michael are inadequate to explain the data just recorded, and they fail to account for the photochemical observations of Klinger.

The conversion of benzil into benzilic acid, therefore, is accurately represented by the equation,



This equation, however, is purely qualitative; for it is obvious from the experimental results that the reaction does not reach completion, and that some as yet unrecognized factor is impeding it.

Is the Benzil Rearrangement Reversible?

The heats of combustion of benzil and of benzilic acid are almost identical (1625 and 1619 Cal. respectively). The change in free energy during the rearrangement must therefore have a very low value, and from this point of view the reversal of Equation 1 does not appear at all improbable. Such a reversal would have considerable significance. For this reason, the conflicting data thus far obtained are given here, in the hope that they may eventually lead to a solution of this problem.

Three g. of imported benzilic acid was refluxed with 1 liter of water for 2 days. After the solution had been rendered alkaline, ether extraction gave 0.08 g. of benzil, m. p. 90°. But another sample of the same lot, not previously refluxed with water, was found to contain 0.06 g. of benzil. Therefore, a portion of this benzilic acid was carefully purified. It was first dissolved in a slight excess of potassium carbonate solution, and this solution was extracted with ether. The alkaline solution was evaporated, and the crystals of potassium benzilate were recrystallized. This purified salt was then precipitated fractionally (1) with dil. acetic acid, (2) with conc. acetic acid, (3) with hydrochloric acid. All 3 fractions melted sharply at 149.5°. This material was used for all further experiments.

As it was possible that the imported material was originally pure, but had slowly reverted (it was at least 8 years old), a weighed portion of the purified product was heated in a sealed tube to 100° for 10 days. Its acidity was then found to be unchanged, so that no benzil could have been formed under these conditions.

Three separate portions of 1.0 g. each were refluxed with water for 3 days. Ether extraction of two of these gave mere traces of oil; in the third case, 0.03 g. of benzil melting at 87° was obtained, which after recrystallization melted at 92°. In this instance, the yellow crystals of benzil were noted in the reflux condenser on the second day.

This result has not been obtained again. Two further trials, with longer boiling, gave small yields of benzophenone, with no visible content of benzil. The benzophenone was converted into its oxime, which melted sharply at 140°, and could have contained but little impurity. Furthermore, no benzil was observed when benzilic acid was

boiled in the presence of an equivalent amount of hydrochloric acid; the same was true when the benzoic acid was partly or almost wholly neutralized.

Thus, the behavior of benzoic acid is seen to be erratic, and subject to influences which have so far escaped observation. This is clearly shown in the following series of data.

The Change from Benzoic Acid to Benzophenone.

A large volume of a nearly saturated solution of benzoic acid was prepared. Five hundred cc. of this required 36.2 cc. of 0.1 *N* alkali for neutralization at the boiling point, with phenolphthalein as an indicator, and 36.1 cc. at room temperature. Both solution and alkali were therefore free from carbon dioxide within the limit of experimental error. Benzoic acid in this concentration is not appreciably volatile with steam; 500 cc. was boiled briskly for 15 minutes, and then titrated; 36.0 cc. of alkali was needed. The normality of this stock solution was 0.00724, equivalent to 1.650 g. of benzoic acid per liter.

Seven portions of 500 cc. each were sealed in Pyrex flasks, and heated at 105° for the periods of time shown below. Flasks 3 to 7 were heated simultaneously. After cooling to room temperature, the flask contents were titrated directly. Very uneven results were obtained.

Flask	Time Days	NaOH Cc.	Total %	Acidity lost per day %
1	2	34.8	3.9	1.9
2	2	35.2	2.8	1.4
3	3	34.7	4.3	1.4
4	5	31.9	11.9	2.4
5	5	34.8	3.9	0.8
6	5	31.7	12.5	2.5
7	5	34.6	4.4	0.9

The contents of Flasks 1 and 2 were combined after neutralization, and extracted carefully with ether. This gave an oily residue, weighing when dry 0.045 g.; calc. for benzophenone, 0.044 g. The contents of Flasks 4 and 6 were cloudy when cool. From 4 there was obtained 0.069 g. of oxime melting at 140° (calc., 0.085 g.), a recovery of 81%. The contents of Flasks 5, 6 and 7 combined gave 0.15 g. of oxime, melting at 138° (calc. 0.14 g.).

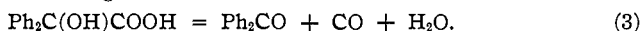
In several instances, during this work on benzoic acid, the ether extracts gave a strong color reaction for benzohydril with sulfuric acid, but no benzohydril was actually isolated at any time. A control test, to see whether by chance benzohydril could form benzophenone oxime with hydroxylamine, was negative.

When exposed to sunlight for 15 days, 500 cc. of the same benzoic acid solution used only 27.5 cc. of sodium hydroxide solution, a loss of 22%. The oxime melted at 118° and carried an oily admixture; after recrystallization, it melted at 139°.

The above data, despite the irregularity observed as to rate, clearly show that the formation of benzophenone is proportional to the loss in acidity which is suffered by the benzoic acid. The reaction therefore cannot be represented by



Klinger and Standke,¹¹ who have studied the decomposition of benzilic acid by prolonged heating to 180°, found that the chief reaction is



This equation also represents the behavior of the acid when it is boiled with water.¹²

There is no likelihood that formic acid is first formed according to Equation 2, and that it immediately breaks down *completely* into water and carbon monoxide. Dr. Branch has been kind enough to calculate that at least 10 times as much formic acid as could be produced in the above experiments would be in stable equilibrium with water and carbon monoxide.¹³

These data leave no room for Nef's hypothesis that benzil is converted into benzilic acid *via* benzophenone and "dioxymethylene." The series of events is, Benzil \rightarrow Benzilic acid \rightarrow Benzophenone, and not Benzil \rightarrow Benzophenone \rightarrow Benzilic acid.

The Mechanism of Rearrangement.

No one of the four "explanations" of the benzil rearrangement that have received serious attention is capable of accounting for the facts recorded above. During the course of this experimental study, a working hypothesis has been developed which has the practical merit of grouping many diverse processes under a single point of view, and of suggesting new modes of approach such as have just been described. Previous investigators have devoted their attention chiefly to abnormal readjustments in the carbon chain—abnormal because infrequent and contrary to the teachings of structural theories—and have overlooked the features which these rearrangements have in common with other reactions, in which no alteration of the carbon chain is involved.

The benzil conversion, like that of pinacol, and like that of dihydroxytartaric acid, is not only a rearrangement, but also an intramolecular oxidation-reduction process.¹⁴ If we permit ourselves to make one single assumption, all of these diverse reactions and with them many others, find a simple explanation.

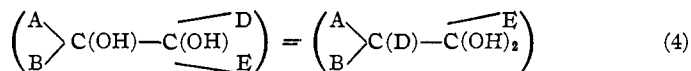
¹¹ Klinger and Standke, *Ber.*, **22**, 1213 (1889).

¹² The amount of carbon monoxide formed is so small, under the conditions of the above experiments, that extremely careful gasometric methods would be required to show accurate proportionality. 500 cc. of benzilic acid solution was boiled as before, after pumping out air as much as possible. After 5 days, during which time the apparatus was sealed, the gases were pumped out again. 8.3 cc. was obtained, of which 6.7 cc. was absorbed by cuprous chloride. The benzilic acid solution had lost acidity equivalent to 2.7 cc. of 0.1 *N* sodium hydroxide solution.

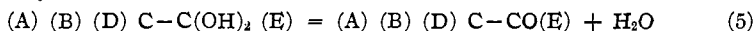
¹³ Branch, *THIS JOURNAL*, **37**, 2316 (1915).

¹⁴ Michael has indeed attempted to bring both rearrangement and intramolecular oxidation under one point of view; but his assumptions as to the rôle played by reagents and solvents are out of harmony with the facts recorded above.

This assumption is that hydroxyl groups attached to adjacent carbon atoms tend to unite with *one* of these carbon atoms and, in so doing, the mobile hydroxyl group exchanges places with some other atom or radical. The typical equation of this process is,



followed by loss of water,



The assumption of a mobile hydroxyl group is not new. Lieben¹⁵ was among the first to suggest it for the pinacol rearrangement. There seems, however, to have existed a strong prejudice against the assumption of mobility for anything except hydrogen. Michael, in his recent critique, did not mention Lieben's hypothesis. Tiffeneau dismissed it somewhat satirically.¹⁶ Meerwein,¹⁷ whose recent work has brought out evidence strongly corroborative of the views here set forth, gave it some thought, but could not find in it a sufficient degree of "Notwendigkeit," and therefore adopted the views of Tiffeneau; but he expressed his conviction that the pinacol rearrangement was an "immediate" process, without any intermediates whatever.

It is clear that under favorable conditions, rearrangements involving merely an exchange of hydroxyl with some other group, might be expected to occur by heating a substance without any reagents whatever, for a long enough period and to a sufficiently high temperature. In the case of sodium dihydroxy-tartrate, a few days at room temperature suffice, as does a single hour at 150°. The behavior of hydrated benzil has just been described. The pinacols rearrange under the influence of heat alone.¹⁸ The transformation of tartaric acid into pyruvic acid has been explained by Chattaway and Ray¹⁹ as an exchange of hydrogen and hydroxyl; this is a typical intramolecular oxidation-reduction reaction, and is induced by moderate temperature increase.

It is not possible, with our present knowledge, to form any definite conception of the *driving force* in these intramolecular processes. In the case of the pinacols, rearrangement is greatly facilitated by dehydrating agents; and it might have seemed as if the free energy of the formation

¹⁵ Lieben, *Monatsh.*, **23**, 63 (1902).

¹⁶ Tiffeneau's phrase is "une sorte de chassé-croisé."

¹⁷ Meerwein, *Ann.*, **396**, 209 (1913); **419**, 121 (1919).

¹⁸ This statement regarding the pinacols is at variance with the published reports of Thorner and Zincke. Professor T. D. Stewart is now investigating the question experimentally.

¹⁹ Chattaway and Ray, *J. Chem. Soc.*, **119**, 34 (1921). They were investigating the well-known dry distillation of tartaric acid. I have since found that *solutions* of tartaric acid in water yield pyruvic acid and carbon dioxide steadily on prolonged boiling.

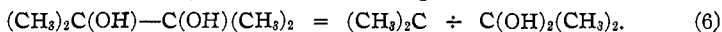
of water were the sufficient as well as the necessary factor. But Vorländer²⁰ has shown that dilute solutions of weak organic acids, which can hardly be classed as dehydrating media, will bring about pinacolone formation; and it has been shown, that the benzil rearrangement takes place with the *addition* of water. We must therefore distinguish between water *formation* as a causing factor, as in ester synthesis, and water *separation* as an incident, as in the pinacols.

The most striking feature of these rearrangements, from the standpoint of affinity problems as well as of atomic structures, is that perfectly symmetrical compounds, such as pinacol, benzil, tartaric acid, dihydroxy-tartaric acid and oxalic acid, represent, in fact, unstable equilibria. When we come to know why such structures are unstable, we shall know what is the cause of rearrangement. Meanwhile, we must be satisfied with the somewhat awkward phrase "intramolecular oxidation and reduction."²¹

Rearrangements of carbon chains, as viewed here, are merely a special case of a general phenomenon. If, in Equation 4, one of the groups A, B, D, E, is hydrogen, that will usually be the one to exchange places with hydroxyl. If no hydrogen is so present, a radical such as methyl, phenyl or carboxyl will shift to take the place of the mobile hydroxyl.

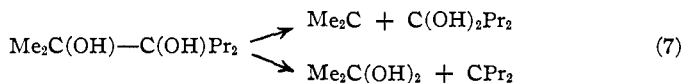
If the compound (COH)₂ABDE is symmetrical, only one "metaklinic" product can result; but if it is unsymmetrical, two or more may be expected. Meerwein's latest work has proved this in convincing fashion, setting a standard of experimental completeness worthy of emulation.

The following convention is suggested for the formulation of such shifts, using the pinacol rearrangement as an example.



The division sign is used to indicate that an hydroxyl group has moved (in this case to the right) and that the vacant bond will be occupied by a shift from that side.

Meerwein has found that in dimethyl-dipropyl glycol the shift occurs in two directions; and, as might be expected from the close resemblance between methyl and propyl, in nearly equal proportions.



Similar results were found by him in the case of dimethyl-dibutyl glycol.²²

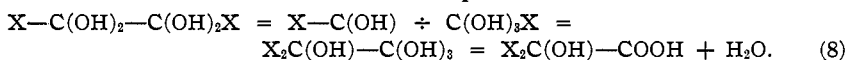
²⁰ Vorländer, *Ber.*, 30, 2266 (1897). For a discussion of this phase of the rearrangement problem, cf. Michael, *Ref.* 5, p. 802.

²¹ A short word may prove desirable. The verb *metaklinomai* (Gr.) (to shift cargo from one side to another) offers an apt analogy. We may speak of *metakliny* or of the *metaklinic* process.

²² The observed proportion of methyl shift to propyl shift is 10:8; of methyl to butyl, 7:4. Meerwein is studying the factors that determine preference in shifting. Tiffeneau, who has done valuable work in this same field, found that in most cases

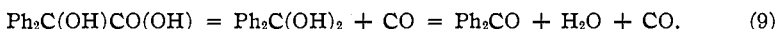
Experimental studies in the field of rearrangement are greatly complicated by the occurrence of side reactions. These may be of the most diverse sort; chief among them is a tendency to rupture the bond connecting the carbon atoms to which the hydroxyl groups are originally attached. This rupturing process may at times become the main reaction, with rearrangement greatly subordinated; such seems to be the case with the aromatic pinacols.²³

Coming now to the consideration of the benzil rearrangement, we may for the present assume that each of the carbonyl groups is capable of adding water, in analogy with dihydroxy-tartaric acid. Using X to represent either phenyl or carboxyl, we may use a single set of equations for the behavior of both of these compounds.



It is an advantage of this method of formulation that it indicates the nature of the rupture products as well. Benzil is ruptured to give benzoic acid and benzaldehyde; dihydroxy-tartaric acid yields oxalic and glyoxalic acids.

The decomposition of benzilic acid described above may be accounted for in similar fashion, as a combination of shift and rupture.



It would require far too much space to point out the wide applicability of the reactions typified by Equations 6, 8, and 9. A very few illustrations will suffice. The formation of acrolein on heating glycerine is an exchange of hydrogen and hydroxyl. The interconversion of glucose, mannose and fructose is an addition of water to the carboxyl group, followed by exchange of hydrogen and hydroxyl. The formation of methylglyoxal from glucose may be accounted for by the shift of 2 hydroxyl groups, followed by rupture. The conversion of methylglycol into a mixture of acetone and propionic aldehyde is a shift of hydroxyl in 2 directions, quite similar to Meerwein's results in the more complicated glycols. The breakdown of benzoyl-formic acid into carbon monoxide and benzoic acid, and of oxalic acid into carbon monoxide and carbonic acid, are analogous to the decomposition of benzilic acid.

phenyl is more labile than methyl. Tiffeneau, however, has not been consistent in developing the quantitative side of this phenomenon. It may be possible some day to establish a "metaklinic" series indicating the relative ease of shift of the various radicals. Hantzsch has done something like this in the case of the Beckmann rearrangement.

²³ Benzyl ether (Cannizaro, *Ann.*, **92**, 113 (1854); Lowe, *ibid.*, **241**, 374 (1887)), on heating, breaks down into benzaldehyde and toluene: $Ph-CH_2-O-CH_2-Ph = PhCHO + PhCH_3$. This reaction is now being investigated; it seems to offer an opportunity for the quantitative study of "metakliny," free from the complications caused by side reactions.

Conclusion.

The electronic conception of intramolecular oxidation and reduction accounts for the phenomena just described, by stating that the oxidized carbon atom loses, and the reduced carbon atom gains, an electron. From this point of view, electron movement and hydroxyl movement are reciprocal; and it may well be that they stand to each other in the relation of cause and effect.

It is difficult, however, to derive any helpful suggestions from this source, in the present state of our information; and it seems more useful to adhere to the established customs of structural interpretation. When we know more about the behavior of the electrons of carbon, there will be no difficulty in re-interpreting the facts of rearrangement.

Meanwhile, we can state only as experimental facts, the comprehension of which escapes us, that if two (or possibly more than two) carbon atoms in a compound are in a symmetrical or in a similar state of oxidation, such a structure is unstable; that one of these carbon atoms tends to a greater degree of oxidation, the other becoming reduced; that this tendency is enhanced by an increase of temperature, and may be greatly accelerated by a variety of catalysts; and that the forces concerned in or released by it are powerful enough, at times, to overcome the forces that bind carbon atoms together.

I must acknowledge my heavy indebtedness to Professors Stewart, Porter and Branch, of California, and to Professor Stieglitz, of Chicago, for their helpful suggestions and still more helpful criticism during the preparation of this paper.

Summary.

1. Benzil is converted into benzilic acid by boiling with water.
2. The action of very weak alkali differs from that of water only by being somewhat faster, but by no means in proportion to the increase in hydroxyl ions.
3. The reversal of the benzil rearrangement is not unlikely, but has not yet been accomplished.
4. Benzilic acid, on boiling with water, yields benzophenone and carbon monoxide.
5. The previous theories of rearrangement do not account for the observed facts.
6. A theory of rearrangement is offered, based upon the forces concerned with intramolecular oxidation and reduction.
7. This theory brings a wide variety of facts into relation with one another.

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