On the Behavior of Benzoyl Carbinol towards Alkalies and Oxidizing Agents.

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS
OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

DEPARTMENT OF CHEMISTRY.

BY

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Zincke and his students were the first to study the behavior of benzoyl carbinol towards oxidizing agents.[1] They found that it gives, according to the oxidizing agent used, varying proportions of mandelic, benzoylformic, benzoic and carbonic acids. The most notable of their experiments was the action of copper and sodium hydroxides on benzoyl carbinol and acetolacetate, r-mandelic and r-lactic acids, respectively, being the chief reaction products obtained. Zincke suggested[2] that in this reaction the benzoyl carbinol might first be resolved into benzaldehyde and formaldehyde and that these products might subsequently combine to give r-mandelic aldehyde, whose conversion to the corresponding acid, in the presence of the oxidizing agent, would then be readily understood. He also presented the view that the aldehyde of benzoyl carbinol might first be formed by direct oxidation of the primary alcohol group present in benzoyl carbinol and that the resulting benzoylformaldehyde might be converted to mandelic acid by intramolecular oxidation and reduction,[3]

$$O : C(C_6H_5)CH : O + H_2O \longrightarrow C_6H_5CH(OH)COOH.$$

Kling, in his recently published statement,[4] divides the action of oxidizing agents into three categories, according to the relative amount of lactic, acetic and carbonic acids obtained from the analogous acetyl carbinol.

It is clearly evident from the work of Nef[5] that mandelic and lactic aldehydes cannot be isolated as such, but are transformed spontaneously into the isomeric benzoyl and acetyl

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[1] Ber. d. chem. Ges., 13, 635. Ann. Chem. (Liebig), 216, 311.
[2] *Ibid.*, 216, 314.
[3] Cf. V. Meyer: Ber. d. chem. Ges., 13, 2344.
[4] Bull. Soc. Chim., [3], 33-34, 1,49. Compt. rend., 139, 740-742.
[5] Ann. Chem. (Liebig), 335, 247-279.

carbinols, which are not tautomeric compounds. Furthermore, the conversion of benzoyl or acetyl carbinol into *r*-mandelic or *r*-lactic aldehyde by dissociation and subsequent addition, as assumed by Zincke (see above) is excluded, as Néf has shown that an equimolecular mixture of formaldehyde and acetaldehyde gives absolutely no *r*-lactic acid in the presence of cupric hydroxide and sodium hydroxide. Nef, therefore, came to the conclusion that benzoyl- and acetylformaldehydes, respectively, must first be formed in the reaction under discussion and that the conversion of the resulting aldehydes into lactic and mandelic acids is due to a benzilic acid rearrangement. As is well known, almost all orthodicarbonyl compounds,

$$\begin{array}{c} XC:O \\ | \\ YC:O \end{array},$$
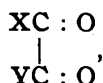
whether in open chains or closed cycles, undergo such a rearrangement or conversion, by absorption of 1 molecule of water, into α-hydroxy acids,

$$XYC(OH)COOH.$$

In some cases, as with hexaketomethylene and diketosuccinic acid, this rearrangement takes place quantitatively in dilute aqueous solution; in most instances it requires the presence of more or less concentrated aqueous caustic alkalies, or at times even solid potassium hydroxide at higher temperatures. Nef[1] has presented the following interpretation of this remarkable rearrangement: The orthodicarbonyl compound $\begin{array}{c} XC:O \\ | \\ YC:O \end{array}$ dissociates into $XYC:O$ and $\diagup\!\!\!\diagdown C:O$; the products of dissociation, in their active molecular form

$$XYC\!-\!O \;+\; \diagup\!\!\diagup C:O,$$
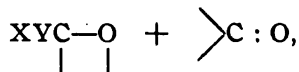
unite to form the addition product,

[1] Ann. Chem. (Liebig), **335**, 272–273.

$$X \diagdown C \text{———} C : O,$$
$$Y \diagup$$

with the O above the triangle structure
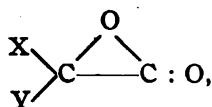
which then, by hydrolysis, gives the α-hydroxyacid

$$X \diagdown C \text{—} O\text{—} C\text{—} + H \cdot OH \rightarrow XYC(OH)COH.$$
$$Y \diagup$$
$$O \qquad\qquad\qquad\qquad O$$
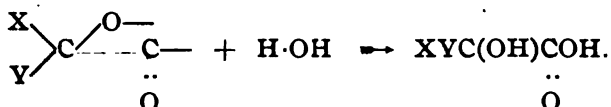
At the suggestion and under the supervision of Professor J. U. Nef I have taken up a careful and exhaustive quantitative study of the behavior of benzoyl carbinol towards oxidizing agents under the most varied conditions. The work of Nef during the past 10 years on the monoatomic alcohols, alde-hydes and fatty acids, as well as on glycols, glycerols and sugars, has shown that it is possible to follow, rigidly, by ex-periment, the course taken by many apparently complicated oxidation processes. The problem in the benzoyl carbinol series seemed especially susceptible of experimental treatment ; first, because the possible acid oxidation products, benzoic, r-mandelic and benzoylformic acids were all well-known, crys-talline compounds, and quantitative methods for their sharp separation could easily be worked out ; second, because the first possible oxidation product of benzoyl carbinol, namely, benzoylformaldehyde was known, having been discovered by v. Pechmann,[1] and its behavior on oxidation could, conse-quently, be carefully investigated. These expectations were in every way realized ; my experiments prove, in a most rigid manner, the correctness of all the conclusions reached by Nef, as briefly presented above. Of special importance is the be-havior of benzoylformaldehyde under various conditions. This substance is converted quantitatively into r-mandelic acid, very rapidly at ordinary temperatures, by all soluble caustic alkalies, even in most dilute aqueous solutions, and also by aqueous copper acetate solutions at 70°–100°. The be-havior of benzoylformaldehyde towards various oxidizing agents alone and in the presence of dilute caustic alkalies

[1] Ber. d. chem. Ges., 29, 2904 ; 22, 2556.

proves, in a most convincing manner, that this substance, in the process of transformation into r-mandelic acid by a benzilic acid rearrangement, must first be dissociated into benzaldehyde and carbonic oxide, as assumed by Nef. The facts are these: A. Benzoylformaldehyde gives, with freshly precipitated mercuric or silver oxides, alone or in the presence of caustic alkalies, benzoic and carbonic acids only; separate experiments with mandelic and benzoylformic acids and the oxides named prove that this oxidation cannot possibly have taken place with the intermediate formation of these acids. B. Benzoylformaldehyde, with cupric oxide and caustic alkalies, as well as with potassium ferricyanide and potassium hydroxide, gives, practically, r-mandelic acid *only*. C. Benzoylformaldehyde, with aqueous potassium permanganate, in the cold, gives, practically, only benzoic acid; under the same conditions, but in the presence of caustic alkalies, about equal amounts of benzoylformic, benzoic and carbonic acids are formed. It is, moreover, certain that the benzoylformic acid is formed from r-mandelic acid obtained by a benzilic acid rearrangement of the aldehyde, and not through a direct oxidation of the aldehyde, and its proportion undoubtedly varies with the concentration of the alkali used.

The only possible interpretation of the results, A, B and C, is the following:

I. Benzoylformaldehyde is partially dissociated into carbonic oxide and benzaldehyde,

$$O:C(C_6H_5)CHO \rightleftarrows C_6H_5CHO + C:O.$$
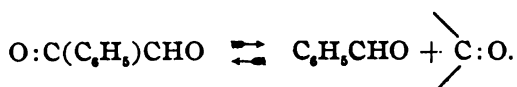
II. The relative rate of transformation of the products of dissociation I into r-mandelic acid,

$$C_6H_5CH.O + C:O \rightarrow C_6H_5CH-\!\!-\!\!C:O, \text{ etc.,}$$
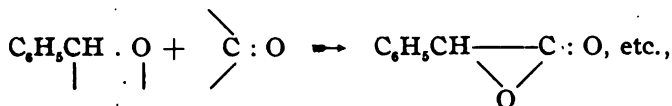
and the relative rate of oxidation of these dissociation products into benzoic and carbonic acids varies in cases A, B and C, re-

spectively. In other words, benzaldehyde and carbonic oxide, reacting, as is known, very readily with the oxides of mercury and silver, are entirely oxidized in the presence of these reagents before they can unite to form r-mandelic acid (case A).

In the presence of alkalies and cupric hydroxide or potassium ferricyanide, on the other hand, since these are very mild oxidizing agents, *only* a benzilic acid rearrangement takes place, *i. e.*, the formation of r-mandelic acid (case B). If potassium permanganate, without alkalies, is used on benzoylformaldehyde no rearrangement to r-mandelic acid occurs, but with alkalies present (case C) about 50 per cent of oxidation of its dissociation products and 50 per cent of transformation to r-mandelic acid takes place. This is not surprising, since in oxidation by potassium permanganate,

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3O,$$
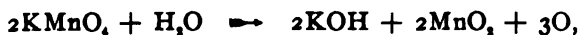
the amount of alkali set free in the reaction is only sufficient to form salts with the benzoic and carbonic acids which are formed; no experiments were carried out to determine the velocity of the transformation of benzoylformaldehyde into r-mandelic acid with varying concentration of the alkali.

These results, therefore, establish experimentally the correctness of Nef's interpretation of the benzilic acid rearrangement; there are, furthermore, numerous observations in the literature which prove that many ortho or 1,2-dicarbonyl compounds undergo dissociation into carbonic oxide and a monocarbonyl derivative at comparatively low temperatures, and this must also be considered as evidence pointing to the same conclusion. Thus benzil and diketosuccinic ester readily decompose, at 250°–300°, into carbonic oxide, benzophenone and ketomalonic ester, respectively.

EXPERIMENTAL PART.

Preparation of Benzoyl Carbinol.—Owing to the extreme sensitiveness of benzoyl carbinol, especially towards alkaline reagents, the methods heretofore used in its preparation[1] were found to give very unsatisfactory yields; the same is true

[1] Graebe: Ber. d. chem. Ges., 4, 34. Hunnius: *Ibid.*, 10, 2910. O. Fischer and Busch: *Ibid.*, 24, 2680. Zincke: Ann. Chem. (Liebig). 216, 306.

when bromacetophenone or α-bromphenylacetaldehyde are digested with potassium formate and methyl alcohol, methods which give acetol quantitatively with the corresponding derivatives in the fatty series.[1]

The hydrolysis of benzoyl carbinol acetate by means of 17 parts of boiling water, for 12 hours, was finally found to be the best means of preparing this substance ; bromacetophenone was made from 75 grams of acetophenone, according to the directions of Möhlau[2] and the crude oil, 124 grams, precipitated by water, was converted into the acetate by digesting for 3 hours, under a reversed condenser, at 125°–130°, with 310 grams of glacial acetic acid and 100 grams of fused sodium acetate. One hundred grams of crude acetate were thus obtained by addition of water, extraction with ether and removal of the acetic acid by washing with sodium carbonate solution ; on distillation under 10–15 mm., 5.3 grams of this boiled below 130° and the remainder, 89 grams, 80 per cent of the theoretical, at 145°–155°, leaving 5 grams of tar in the distilling flask. On hydrolysis of the main fraction of the acetate, as mentioned above, 49 grams of pure benzoyl carbinol, crystallized from ether-ligroin and melting at 85°–86°, were obtained, besides 3.5 grams of tar, insoluble in boiling water. Benzoyl carbinol boils, according to the observations of Nef, without the slightest decomposition, at 118°–120° (11 mm.) ; on distilling 10 grams of it, under 10 mm. pressure, through a combustion tube filled with pumice, kept at 400°–440°, in a 28 burner furnace, 7 grams of carbinol were recovered unchanged (time, 10–15 minutes) ; on repeating the experiment, but raising the temperature to 580°–600°, much decomposition with gas evolution took place. The liquid decomposition products, 2.50 grams, were proved to contain benzene and benzaldehyde, which was identified as phenylhydrazone ; 0.80 gram, m. p. 158°, was obtained. A strong odor of formaldehyde was noticed in the apparatus. This proves that benzoyl carbinol dissociates, by heat, in a manner analogous to acetol,[3] into benzaldehyde and formaldehyde,

[1] Ann. Chem. (Liebig), 335, 260, 265.
[2] Ber. d. chem. Ges., 15, 2464.
[3] Nef : Ann. Chem. (Liebig), 335, 250.

$$C_6H_5COCH_2OH \longrightarrow C_6H_5CHO + H_2C:O.$$

Action of Benzoyl Carbinol on Copper Salts.—In the cold the first stage in the action of aqueous copper acetate and copper sulphate, respectively, on benzoyl carbinol is the conversion into benzoylformaldehyde, as was proved by special experiments; in the former case cuprous oxide is formed and in the latter metallic copper is deposited. It is extremely probable that, in both cases, there is first an intermediate formation of cupric benzoyl carbinol,[1] and this, like all salts of primary and secondary alcohols, has a much lower dissociation point than the corresponding alcohol; consequently the following reaction takes place:

$$(C_6H_5COCH_2O)_2Cu + 2H_2O \longrightarrow$$

$$2C_6H_5COCH + Cu(OH)_2 + 2H \cdot OH \longrightarrow$$

$$2C_6H_5COCH(OH)_2 + 2H + Cu(OH)_2.$$
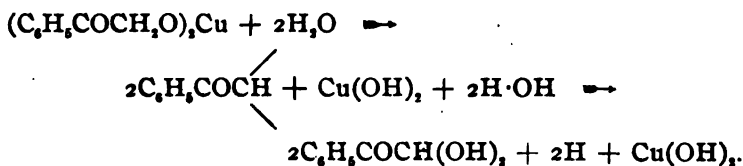
The atomic hydrogen thus formed then reduces the cupric salt present either to metallic copper or to the cuprous state.

Benzoyl Carbinol and Cupric Acetate.—Five grams of benzoyl carbinol, dissolved in 120 cc. of warm water, were added to a solution of 22 grams (3 mols.) of crystallized copper acetate, in 350 cc. of water; the temperature of the resulting solution was at first 35° and cuprous oxide began to separate out almost immediately. The mixture was allowed to attain room temperature and was then left standing for 14 days. The precipitate of cuprous oxide was found to weigh 3.5 grams and the aqueous filtrate was extracted 18 times with ether. The oily residue, obtained on evaporating the moist ether extracts, was freed from acetic and other acids by digestion with water and 4 grams of calcium carbonate; the aqueous filtrate, again extracted thoroughly with ether, yielded, on evaporation of the moist ether and on drying over sulphuric acid *in vacuo*, 3.9 grams of a neutral, crystalline, pungent smelling substance,

[1] Nef: Ann. Chem. (Liebig), **335**, 275.

melting at 70°; on crystallizing from water it melted at 78° and remained unchanged when mixed with an equal amount of v. Pechmann's[1] benzoylformaldehyde monohydrate. The identity of the product obtained with benzoylformaldehyde was furthermore established by the following tests:

a. One-half gram, dissolved in 40 cc. of water, was treated with 0.2 gram of powdered calcium hydroxide, in the cold; the solution turned yellow at once and after standing 12 hours gave, on acidifying with hydrochloric acid and thorough extraction with ether, 0.5 gram of *r*-mandelic acid, m. p. 118°.5.

b. One-half gram of the aldehyde, dissolved in 4 cc. of 50 per cent alcohol gave, on addition of 0.05 gram of potassium cyanide and subsequent addition of water, 0.3 gram of the yellow benzoin derivative of benzoylformaldehyde,

$$C_6H_5COCH(OH)COCOC_6H_5,$$

first obtained by Söderbaum;[2] the melting-point of this product was found to be 180°, with previous darkening at 176°, whereas Söderbaum found 170°.

c. The benzoylformaldehyde obtained on treatment with Fehling's solution does not give the slightest reduction to cuprous oxide. This is in harmony with v. Pechmann's observation; with silver oxide, on the other hand, a reduction to metallic silver takes place at higher temperatures (see below). Since pure benzoylformaldehyde and benzil are without action on Fehling's solution, it is very probable that other pure orthodicarbonyl compounds, such as glyoxal, acetylformaldehyde and diketosuccinic acid, must behave in a similar manner towards this reagent, as it must simply transform the compounds, by a benzilic acid rearrangement, into the corresponding α hydroxy acids. I therefore conclude that acetylformaldehyde, which is the perfect analogue of benzoylformaldehyde in the fatty series, and which has recently been isolated by Harries and Turk,[3] must have contained some impurity, as the product obtained by them is described as reducing Fehling's solution. Finally, it should be mentioned that, in addition to

[1] Ber. d. chem. Ges., 22, 2557.
[2] *Ibid.*, 24, 1381, 3038.
[3] *Ibid.*, 38, 1630.

the main neutral reaction product obtained in the experiment above described, the aqueous solutions containing lime salts of acids gave, when worked up by the method described below, 0.15 gram of benzoic acid, m. p. 121°, and 0.35 gram of mandelic acid, m. p. 118°, but no trace of benzoylformic acid.

Benzoyl Carbinol and Copper Sulphate.—No action was noticed on mixing cold, aqueous solutions of 5 grams of benzoyl carbinol and 18.2 grams (2 mols.) of crystallized copper sulphate, the total volume being 400 cc., but on allowing the mixture to stand outdoors in the sunlight, for 2.5 months, the solution had changed to dark green, the action being accompanied by a deposition of copper. It was now warmed for 6 hours at 50°–60°, finally, for a short time, at 100°, and then filtered from the copper, 1.10 grams. The aqueous filtrate was extracted with ether and the reaction products separated into acid and neutral portions, as mentioned above, by powdered calcium carbonate. There were obtained, as reaction products, 2.7 grams of benzoylformaldehyde monohydrate, melting at 78°, containing traces of unchanged carbinol, and 0.5 gram of *r*-mandelic acid, melting at 118°.5, besides 0.25 gram of benzoic acid.

The quantitative separation and determination of the relative amounts of benzoic, benzoylformic and *r*-mandelic acids formed in the various cases was always carried out as follows : the acid mixture was first distilled with steam, which carried over only benzoic acid. The non-volatile portion was then treated with phenylhydrazine, dissolved in an equal volume of 50 per cent acetic acid and, after 24 hours' standing, benzoylformic acid phenylhydrazone separated out completely. It was purified by dissolving in dilute sodium carbonate solution, reprecipitating by dilute sulphuric acid and crystallizing from hot benzene.[1] From this the amount of keto-acid present could be determined by calculation. The aqueous filtrate from the phenylhydrazone, containing only *r*-mandelic acid, was worked up for this acid by thorough extraction with ether and subsequent washing with dilute sulphuric acid. The residue, after the evaporation of the ether, was heated at 100° (25–30 mm.)

[1] Cf. Nef: Ann. Chem. (Liebig), **280**, 295.

in order to remove the acetic acid. The *r*-mandelic acid was finally crystallized from a mixture of ether and ligroin (70°–80°).

The Behavior of Benzoylformaldehyde towards Copper Salts at 100°.—The most striking property of benzoylformaldehyde is its transformation into *r*-mandelic acid, which takes place very rapidly with all aqueous caustic alkalies, even in the cold and in most dilute solutions. This was first observed by v. Pechmann and Söderbaum[1] and has been repeatedly confirmed by me.

The conversion of the aldehyde into *r*-mandelic acid also takes place by heating with aqueous solutions of various copper salts, as is proved by what follows: Two grams of benzoylformaldehyde hydrate and 2.97 grams of crystallized copper acetate, dissolved in 70 cc. of water, were boiled for 1 hour. There was a gradual separation of insoluble greyish-white crystalline copper mandelate.[2] The precipitate was dissolved in dilute hydrochloric acid and, on extracting well with ether as described, 1.7 grams of pure *r*-mandelic acid, m. p. 118°.5, were obtained. A special experiment with a solution of 2 grams of benzoylformaldehyde and 8.10 grams of copper acetate, in 225 cc. of water, proved that, on standing 3 days at ordinary temperatures, no transformation into *r*-mandelic acid had taken place. On extracting the solution 18 times with ether and heating with calcium carbonate in the usual manner, 1.44 grams of aldehyde were recovered unchanged. A solution of 1 gram of benzoylformaldehyde hydrate and 1.25 grams of crystallized copper sulphate, in 100 cc. of water, was heated at 130°, for 7 hours; 0.55 gram of bluish-white copper mandelate precipitated, from which 0.30 gram of the pure acid was obtained. The aqueous filtrate yielded 0.5 gram of oily residue, which was proved to be mainly unchanged aldehyde by conversion into 0.40 gram of pure *r*-mandelic acid, by means of sodium hydroxide.

Special experiments with an aqueous solution of *r*-mandelic acid, containing molecular quantities of copper acetate or cop-

[1] *Loc. cit.*
[2] Ann. Chem. (Liebig), 18, 320.

per sulphate, proved that in both cases there is practically complete precipitation of copper mandelate on warming on a boiling water-bath, acetic and sulphuric acids, respectively, being thus set free.

Benzoyl Carbinol and Copper Salts at 100°.—In view of the results just presented, the following experiment with benzoyl carbinol and aqueous copper acetate needs no further elucidation. A solution of 5 grams of benzoyl carbinol and 22 grams of crystallized copper acetate (3 mols.) dissolved in 425 cc. of water, was heated, after standing 12 hours, first at 50°–60° and finally for 3 hours at 100°. The precipitate, which at first consisted only of cuprous oxide, gradually became covered with cupric mandelate. The total weight was 10 grams and from this, by treatment with dilute hydrochloric acid and extraction with ether, 4 grams of pure mandelic acid were obtained. The aqueous filtrate, acidified with dilute sulphuric acid and extracted with ether, etc., gave 0.10 gram of benzoic acid, melting at 121°, 0.20 gram of *r*-mandelic acid, melting at 118°.5, and a trace of benzoylformic acid.

Benzoyl Carbinol and Cupric and Sodium Hydroxides.—Benzoyl carbinol and acetol, respectively, reduce Fehling's solution very rapidly in the cold. The quantity of oxygen used in the oxidation of the acetol has been determined by W. H. Perkin, Jr.,[1] and others, and found to be 1 atom. It is practically certain, from Zincke's experiments with acetol and benzoyl carbinol,[2] and from the following one with benzoyl carbinol that *r*-lactic and *r*-mandelic acids, respectively, are formed in this oxidation process. Furthermore, the oxidation proceeds through an intermediate formation of acyl-formaldehyde, which then, in the presence of the strong caustic alkali, immediately undergoes a benzilic acid rearrangement.
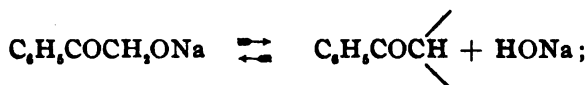
The benzoyl carbinol undoubtedly forms a sodium or potassium salt with the caustic alkali present,[3] which, having a low

[1] J. Chem. Soc., **59**, 788.
[2] *Loc. cit.* Cf. Nef: Ann. Chem. (Liebig), **335**, 273.
[3] Nef: *Loc. cit.*

dissociation point, is relatively much dissociated at ordinary temperatures into benzoyl methylene,

$$C_6H_5COCH_2ONa \rightleftarrows C_6H_5COCH\diagup_\diagdown + HONa;$$

the latter then takes up the hydroxyl ions present, giving benzoylformaldehyde hydrate and the atomic hydrogen or kation thus set free reduces the bivalent copper to cuprous oxide. Since bromacetophenone is also partially dissociated into benzoyl methylene and hydrogen bromide,

$$C_6H_5COCH_2Br \rightleftarrows C_6H_5COCH\diagup_\diagdown + HBr,$$
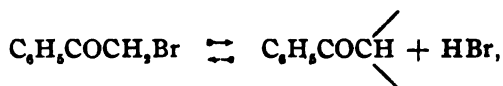
at ordinary temperatures, it is to be expected that this substance must give, with Fehling's solution as well as with sodium and cupric hydroxides, exactly the same results as benzoyl carbinol ; this is proved by what follows : Five grams of benzoyl carbinol, in 310 cc. of water, were added to a solution of 18.10 grams (2 mols.) of crystallized copper sulphate, in 90 cc. of water. On the addition of 8 grams of sodium hydroxide (5 mols.), dissolved in 24 cc. of water, reduction to cuprous oxide took place at once, in the cold. The mixture was finally warmed for 15 minutes on a water-bath, filtered and the yellow filtrate evaporated to dryness under 15–20 mm. pressure (bath 100°). On acidifying with hydrochloric acid and extracting 7 times with ether, a total of 5.15 grams of reaction product was obtained. This gave, by working up in the usual manner, 3.70 grams of r-mandelic acid, melting at 118° ; 0.10 gram of pure benzoic acid and 0.25 gram of benzoylformic acid (from 0.40 gram of the hydrazone).

Bromacetophenone and Cupric and Sodium Hydroxides.—Five grams of bromacetophenone, suspended in a solution of 12.5 grams (2 mols.) of crystallized copper sulphate, in 300 cc. of water, were treated with 10 grams of sodium hydroxide (5 mols.) in 100 cc. of water. On shaking violently, reduction to cuprous oxide took place at once and, after standing in the cold for 24 hours and then working up as in the previous case,

I obtained 2.30 grams of pure mandelic acid, besides 1 gram of unchanged bromacetophenone. When this experiment was repeated at 100°, for 8 hours, only 2.40 grams of crude reaction products were extracted by ether, and from this I obtained 0.50 gram of benzoic acid, 0.41 gram of mandelic acid and 0.25 gram of benzoylformic acid.

Benzoyl Carbinol, Potassium Hydroxide and Potassium Ferricyanide.—Five grams of benzoyl carbinol, dissolved in 300 cc. of water, were added to a mixture of 60.4 grams of potassium ferricyanide and 10.4 grams of potassium hydroxide, in 400 cc. of water, the resulting temperature being 38°. After standing 12 hours, the mixture was worked up by acidifying with dilute sulphuric acid and extracting 6 times with ether. Three and seven-tenths grams of pure mandelic acid, besides 0.30 gram of benzoic acid, were finally obtained. A special experiment with 0.5 gram of benzoylformaldehyde hydrate, dissolved in 25 cc. of water and 18 cc. of a solution containing 3.25 grams of potassium ferricyanide and 0.85 gram of potassium hydroxide, after standing 4 hours in the cold, gave 0.40 gram = 80 per cent of the theoretical amount of pure mandelic acid. It is obvious, therefore, without further comment, that the reactions with benzoyl carbinol and alkaline copper and ferricyanide solutions proceed in a perfectly analogous manner. Finally, a special experiment with 2 grams of mandelic acid, 10.80 grams of potassium ferricyanide, 3 grams of potassium hydroxide, dissolved in 150 cc. of water, proved that, after 24 hours' standing in the cold, no oxidation of the acid had taken place, as 1.80 grams were recovered unchanged by working up in the usual manner.

Acetophenone, Potassium Ferricyanide and Potassium Hydroxide.—According to the literature,[1] acetophenone gives benzoylformic and benzoic acids, by oxidation with the reagents just named. These observations were confirmed and it was proved with special care that no trace of *r*-mandelic acid is formed in this case. This shows that the oxidation reactions with acetophenone cannot possibly proceed in a manner analogous to those of benzoyl carbinol and bromacetophenone ; there was,

[1] Buchka and Irish : Ber. d. chem. Ges., **20**, 389.

a priori, a possibility of this. Five grams of acetophenone were added to a solution containing 68 grams of potassium ferricyanide (2.5 atoms of oxygen), 16 grams of potassium hydroxide and 800 cc. of water. The reaction sets in at once, in the cold ; after 36 hours' standing and filtering from a small amount of yellow, flocculent precipitate, the solution was acidified with dilute sulphuric acid and worked up for acids by extracting with ether, etc. I obtained 1.05 grams of benzoylformic acid, 0.20 gram of benzoic acid, 0.70 gram of tar, but no mandelic acid.

Benzoyl Carbinol and Potassium Permanganate.—A solution of 5 grams of benzoyl carbinol, in 120 cc. of warm water, was slowly added to 7.40 grams of potassium permanganate (3 mols.) dissolved in 300 cc. of water, which was cooled by running water. After 3 hours' standing the excess of permanganate was removed by the addition of alcohol and the colorless filtrate worked as usual for acids. Three and nine-tenths grams of pure benzoic acid, containing no trace of mandelic or benzoylformic acids, were obtained. As mentioned in the introduction, the results are quite different if the oxidation is carried on in the presence of caustic alkalies. Five grams of benzoyl carbinol, in 220 cc. of water, were added, in the cold, to a solution containing 11.60 grams of potassium permanganate (2 mols.) and 2.94 grams of sodium hydroxide (2 mols.), in 200 cc. of water. After 12 hours' standing the aqueous filtrate, when acidified with dilute sulphuric acid and extracted with ether, gave 5.3 grams of crude acid material. This was resolved into 2.3 grams of benzoylformic acid and 1.7 grams of benzoic acid.

Benzoylformaldehyde and Potassium Permanganate. — Two grams of benzoylformaldehyde, in 44 cc. of water, and a solution of 4.16 grams of potassium permanganate (2 mols.) in 75 cc. of water, gave, after standing 3 hours in the cold, 1.5 grams of pure benzoic acid. In an experiment using the same amounts of material as in the one just presented, but having, in addition, 1.04 grams of sodium hydroxide (2 mols.) present, 0.87 gram of benzoylformic acid and 1.2 grams of benzoic acid

were obtained. It is obvious that the benzoic acid formed in the experiment with permanganate alone may come, in the case of benzoyl carbinol, in part from an oxidation of the dissociated portions,

$$C_6H_5COCH_2OH \rightleftharpoons C_6H_5CHO + \overset{\diagdown}{\underset{\diagup}{C}}HOH.$$
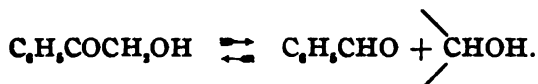
In the presence of caustic alkali, however, as well as in all cases with benzoylformaldehyde, this must be formed *exclusively* from the oxidation of the dissociated benzoylformaldehyde hydrate molecules,

$$C_6H_5COCHO \rightleftharpoons C_6H_5CO + \overset{H}{\underset{\diagup}{\overset{\diagdown}{C}}O.}$$
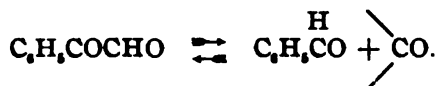
Regarding the formation of benzoylformic acid in the experiments, it is certain that this results from an intermediate transformation of the benzoylformaldehyde by the caustic alkali present into *r*-mandelic acid, which, as will be shown directly, must oxidize at once under the conditions of the experiment to benzoylformic acid.

The formation of benzoylformic acid cannot possibly be ascribed to a *direct* oxidation of the molecular benzoylformaldehyde,

$$C_6H_5COCH(OH)_2 + O \longrightarrow C_6H_5COCOOH + H_2O,$$

because, in that case, this acid should have been obtained from the aldehyde by aqueous permanganate alone and without the formation of any benzoic acid. Special experiments by Buchka and Irish[1] with potassium benzoylformate and an excess of permanganate prove that this acid is absolutely unchanged even after 14 days' standing, and this fact was confirmed. The benzoic acid, which is formed exclusively from benzoyl carbinol, as well as from benzoylformaldehyde with aqueous permanganate must, therefore, come from a burning of these molecules in the dissociated condition. When caustic alkali is present this is still one of the main results, but in that case

[1] Ber. d. chem. Ges., 20, 387. Cf. Beilstein : *Ibid.*, 17, 840.

there is about an equal amount of transformation of the ben-
zoylformaldehyde into r-mandelic acid, which is then at once
further oxidized.

The experiments of Nef[1] have shown very decisively that the
free r-lactic acid is dissociated relatively *more* into acetalde-
hyde and formic acid,

$$CH_3CH(OH)COOH \rightleftharpoons CH_3CHO + HCOOH,$$

whereas the salts of this acid, especially in the presence of
caustic alkalies, which prevent hydrolysis and admit of further
salt formation, are relatively *more* dissociated into water and
ethylidenecarboxylic acid,

$$CH_3CH(OH)COOM \rightleftharpoons CH_3(MOOC)C{<} + H_2O.$$
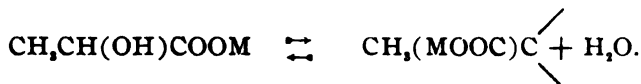
This explains why lactic acid in the free condition, or by the
hydrolysis of its salts, *invariably* gives only acetic, formic and
carbonic acids on treatment with oxidizing agents, and why
the lactates, on the other hand, by the oxidation of the secon-
dary alcohol group, invariably give acetylformic acid only.
My own experiments with the analogous r-mandelic acid have
confirmed in every way these conclusions of Nef and show that
they apply, word for word, in this case also. Beilstein has
shown[2] that r-lactic acid with alkaline permanganate solutions
in the cold, gives a large yield of pyruvic acid. I have found
that r-mandelic acid, under similar conditions, even when a
great excess of alkaline potassium permanganate is added,
gives benzoylformic acid quantitatively. This is, in fact, by
far the best method for preparing benzoylformic acid. It is
important to realize that an excess of alkali should be present,
in which case no trace of benzoic acid can be formed. If free
mandelic acid, or even a mandelate, be treated, in aqueous
solution, with potassium permanganate, there is a chance for
formation of some benzoic acid, because free mandelic acid,
formed by hydrolysis, must be present and this gives, by
oxidation, benzoic and carbonic acids only, because it is disso-
ciated mainly according to the scheme

[1] Ann. Chem. (Liebig), **335**, 296.
[2] *Loc. cit.*

$$C_6H_5CH(OH)COOH \rightleftharpoons C_6H_5CHO + HCOOH.$$
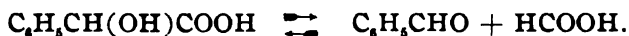
Benzoyl Carbinol and Silver Oxide.—Three grams of benzoyl carbinol, dissolved in 300 cc. of water, were added to 2.25 mols. of freshly precipitated and well washed silver oxide, from 16.8 grams of silver nitrate ; no action takes place until the temperature is raised to 70°. After heating 4 hours on a boiling water-bath, during which time a steady stream of carbon dioxide was evolved, the reduction to silver was complete. One and nine-tenths grams of benzoic acid, 0.30 gram of unchanged carbinol and 10 grams of silver were the only reaction products. In a second experiment, using 4 grams of carbinol, silver oxide from 20 grams of silver nitrate (4 mols.), 4.7 grams of sodium hydroxide (4 mols) and water (total volume 350 cc.), reduction took place rapidly at the ordinary temperature. Pure benzoic acid, 3.32 grams = 92 per cent of the theoretical amount, and 12.60 grams of silver were the only products found.

Benzoylformaldehyde and Silver Oxide.—One gram of benzoylformaldehyde hydrate, dissolved in 75 cc. of water, was treated with 1.25 mols. of freshly precipitated and well washed silver oxide, from 2.52 grams of silver nitrate. No action took place on standing over night. Therefore the mixture was heated for 3 hours, at 70°–100°, when a copious evolution of carbon dioxide was observed. There were obtained 0.75 gram of pure benzoic acid, 92 per cent of the theory, silver and carbon dioxide, as the only reaction products. On repeating the experiment, having, in addition, 1.32 grams of sodium hydroxide (2 mols.) present, a reduction of silver took place at once, in the cold. Eight-tenths of a gram of pure benzoic acid, 1.77 grams of silver and only a few milligrams of *r*-mandelic acid were obtained.

Mandelic Acid and Silver Oxide.—In a special experiment with 1 gram of mandelic acid, 1 mol. of freshly precipitated silver oxide, 0.53 gram = 2 mols. of sodium hydroxide and 50 cc. of water, it was found that no trace of reduction to silver took place on heating for 6 hours on a boiling water-bath ; the acid was, furthermore, recovered entirely unchanged. Two and

eight tenths grams of pure silver mandelate,[1] dissolved in 350 cc. of water and treated on a boiling water-bath for 4 hours, with 2 mols. of freshly precipitated and well washed silver oxide, from 8.10 grams of silver nitrate, gave, on working up in the usual manner, 0.40 gram of benzoic acid, besides 0.55 gram of unchanged r-mandelic acid, but no trace of benzoylformic acid. These results are in harmony with the work of Nef[2] on lactic acid. The observations prove, therefore, with great precision, that no mandelic acid can have been formed as an intermediate product in the action of silver oxide alone, or in the presence of sodium hydroxide, on benzoyl carbinol or benzoylformalde-hyde, respectively.

Benzoylformic Acid and Silver Oxide.—Silver oxide, in the presence of sodium hydroxide, is without effect on benzoyl-formic acid in the cold. On heating to 100°, however, reduc-tion to silver and a quantitative transformation to carbonic and benzoic acids takes place. Thus a mixture of 0.50 gram of benzoylformic acid, 0.52 gram of sodium hydroxide, 1 mol. of silver oxide and 25 cc. of water gave, on heating during 3 hours, at 100°, 0.40 gram of benzoic acid.

One and two-tenths grams of silver benzoylformate, dis-solved in 300 cc. of water containing 1.25 mols. of well washed silver oxide, remained unchanged after 3 hours' heating at 30°, but, on heating at 100°, carbon dioxide began to be evolved and, after 3 hours' heating, 0.50 gram of pure benzoic acid was obtained as a reaction product.

These experiments prove that benzoylformic acid cannot have been formed as an intermediate product in the action of silver oxide alone, or in the presence of caustic alkalies, on benzoyl carbinol or benzoylformaldehyde ; it is certain, there-fore, that the benzoic and carbonic acids obtained in these cases result from a direct oxidation of the dissociation products of benzoylformaldehyde,

$$C_6H_5COCHO \rightleftarrows C_6H_5CHO + \diagdown CO,$$

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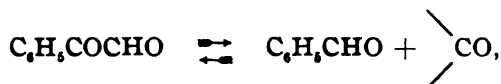
[1] Winckler : Ann. Chem. (Liebig), 18, 310.
[2] *Ibid.*, 335, 277, 297, 315.

which, in these instances, cannot recombine to form *r*-mandelic acid because their speed of oxidation must be far more rapid than the velocity of the benzilic acid rearrangement.

The corresponding experiments, using freshly precipitated mercuric oxide in place of silver oxide, lead to exactly the same conclusions; they are, therefore, simply mentioned here without further comment.

Benzoyl Carbinol and Mercuric Oxide.—Five grams of benzoyl carbinol, dissolved in 350 cc. of water, were treated with an emulsion of freshly precipitated mercuric oxide, from 22 grams of mercuric chloride, in 200 cc. of water. No action took place in the cold, but on heating for 9 hours on a water-bath, much carbon dioxide was evolved. Pure benzoic acid, 3.75 grams = 83 per cent of the theoretical, besides 0.35 gram of unchanged carbinol were obtained as reaction products. In a second experiment, using the same amounts of material, but adding also a solution of 6 grams of sodium hydroxide in 50 cc. of water, reduction to mercury took place at once, in the cold; after 12 hours' standing, 4.10 grams of pure benzoic acid = 91.3 per cent of the theory, were obtained.

Benzoylformaldehyde and Mercuric Oxide.—One gram of benzoylformaldehyde hydrate, dissolved in 75 cc. of water, was treated with 1.25 mols. of freshly precipitated mercuric oxide and thereupon a solution of 0.52 gram of sodium hydroxide (2 mols.) in 25 cc. of water were added. Reduction took place at once, in the cold and, after 12 hours' standing, 0.85 gram (theory 0.88 gram) of pure benzoic acid was obtained, but no trace of mandelic acid.

A special experiment with 2 grams of mandelic acid, 1 mol. of precipitated mercuric oxide and 1.60 grams of sodium hydroxide, in 50 cc. of water, proved that no reduction to mercury took place, even on heating 2.5 hours on a water-bath; 1.90 grams of mandelic acid were subsequently recovered unchanged. Finally, it should be emphasized, that my results with mercuric oxide and benzoyl carbinol are in accord with the corresponding ones obtained by Nef with acetol.[1] Kling[2]

[1] Ann. Chem. (Liebig), **335**, 276.
[2] Bull. Soc. Chim., [3], **33-34**, 1, 49.

states that acetol is converted by mercuric hydroxide *quantitatively* into lactic acid ; this is obviously a mistake.

On the Behavior of Benzoyl Carbinol, Benzoylformaldehyde, Mandelic Acid and Benzoylformic Acid towards Chromic and Dilute Sulphuric Acids.—The following quantitative experiments, which show that these substances give benzoic and carbonic acids only, on oxidation in the cold with chromic acid in dilute sulphuric acid solution, are simply recorded here ; they require no further elucidation :

a. A mixture of 5 grams of benzoyl carbinol, 8.10 grams of potassium dichromate (2.25 atoms of oxygen), 10.8 grams of sulphuric acid and 400 grams of water gave, after standing 2 days in the cold, 2.10 grams of benzoic acid and 1.70 grams of unchanged carbinol.

b. One-half gram of benzoylformaldehyde hydrate, 0.74 gram of potassium dichromate, 0.97 gram of sulphuric acid and 70 cc. of water gave, after 2 days' standing in the cold, 0.44 gram of pure benzoic acid.

c. One gram of mandelic acid, 1.46 grams of potassium dichromate, 5.76 grams of sulphuric acid and 70 cc. of water gave, on standing 24 hours in the cold, 0.75 gram of benzoic acid.

d. One-half gram of benzoylformic acid, 0.41 gram of potassium dichromate, 0.60 gram of sulphuric acid and 50 cc. of water gave, on standing over night in the cold, 0.40 gram of benzoic acid.

PART II.

ON THE BEHAVIOR OF BENZOYL CARBINOL TOWARDS ALKALIES ; A REVISION OF PAAL AND SCHULZE'S WORK ON THE α- AND β-HALOGEN DIPHENACYLS.

On treatment of acetol, with caustic alkalies, under the most varied conditions, Nef never obtained a trace of *r*-lactic acid but mainly neutral, deep red colored resins which were considered by him to be polymerized acetylmethylene resin.[1] Benzoyl carbinol behaves in an entirely similar manner towards caustic alkalies, as well as towards alcoholic potassium hy-

[1] Ann. Chem. (Liebig), **335**, 278.

droxide and sodium ethylate. A small quantity of benzoic acid, entirely free from traces of *r*-mandelic acid, is invariably formed ; the main reaction products, however, consist of dark yellow, non-volatile resins, in which no trace of *cis*- or *trans*-dibenzoylethylene,[1] but at times traces of *trans*-tribenzoylcyclotrimethylene, melting at 295°,[2] were found. The resins obtained could, more-over, never be converted into solids or into crystalline deriva-tives.

Since the monohalogenated acetophenones give, on treat-ment with various reagents, such as sodium acetoacetic ether, ammonia and, especially, with alcoholic potassium hydroxide or sodium ethylate (one-half mol.) large quantities of so-called space isomeric α- and β-halogen diphenacyls,[3] it was thought possible that oxyacetophenone might, on similar treatment, first give the corresponding space isomeric α- and β-oxydiphenacyls ; consequently, attempts were made to obtain these products first by synthesis directly from the so-called α- and β-bromdiphen acyls. Paal and Schulze have made an especially exhaustive study of these two compounds.[4] They find that they are totally different from the *real* γ-bromdiphenacyl,

$$C_6H_5COCHBrCH_2COC_6H_5,$$

obtained from *cis*- and *trans*-dibenzoylethylene and hydrogen bromide. In view of the fact that their products give, by re-duction, small amounts of diphenacyl or its corresponding glycol,

$$C_6H_5CH(OH)CH_2CH_2CH(OH)C_6H_5,$$

and because a fourth isomeric, so-called δ-halogen diphenacyl was isolated, Paal and Schulze give to their α- and β-com-pound the following dienol formula,

$$C_6H_5C(OH) : CBrCH : C(OH)C_6H_5,$$

which is, obviously, capable of giving four different space iso-mers.

[1] Ber. d. chem. Ges., **33**, 3784 ; **35**, 168.
[2] Paal and Schulze : *Ibid.*, **36**, 2425.
[3] Fritz : *Ibid.*, **28**, 3028. Paal and his students : *Ibid.*, **19**, 3146 ; **22**, 3225 ; **28**, 2102 ; **29**, 2092 ; **32**, 530 ; **36**, 2405.
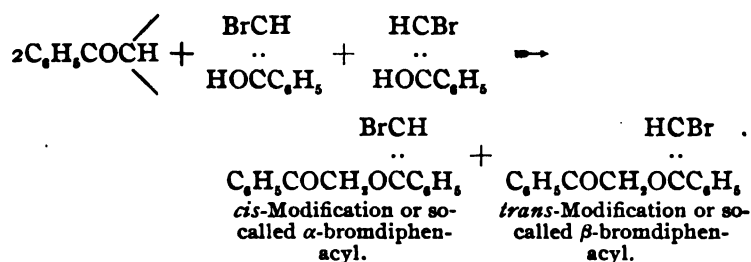[4] Ber. d. chem. Ges., **36**, 2386, 2405, 2415, 2425.

Further consideration shows, however, a great many serious objections to the formulae proposed by Paal and Schulze for their α-, β- and δ-compounds. It is noteworthy, (1) that they were never able to prove the presence of hydroxyl groups in their substances; (2) the compounds do not go over into furfuran derivatives by loss of water; (3) the α- and β-compounds have never been converted into the real γ-bromdiphenacyl, or *vice versa*, nor into one of the space isomeric dibenzoylethylenes.

On the other hand, the real γ-halogen diphenacyls go over quantitatively, even on standing, and especially on heating with sodium acetate and acetic acid, into *trans*-dibenzoylethylene.

In the present state of our knowledge there are, moreover, two other possible interpretations[1] of the reaction between bromacetophenone and sodium ethylate.

I. The benzoylmethylene, resulting from the dissociation of bromacetophenone, may react by alkylation with unchanged bromacetophenone *in the enol form*, and thus give rise to two space isomeric *cis*- and *trans*-α-phenacyloxy-ω-bromstyrols:

$$2C_6H_5COCH \nwarrow\searrow + \begin{array}{c} BrCH \\ \cdot\cdot \\ HOCC_6H_5 \end{array} + \begin{array}{c} HCBr \\ \cdot\cdot \\ HOCC_6H_5 \end{array} \longrightarrow$$

$$\begin{array}{c} BrCH \\ \cdot\cdot \\ C_6H_5COCH_2OCC_6H_5 \end{array} + \begin{array}{c} HCBr \\ \cdot\cdot \\ C_6H_5COCH_2OCC_6H_5 \end{array}$$

cis-Modification or so-called α-bromdiphenacyl.　　*trans*-Modification or so-called β-bromdiphenacyl.

II. The benzoylmethylene might react with the active keto-bromacetophenone molecules present,

$$C_6H_5COCH \nwarrow\searrow + \begin{array}{c} -O \\ | \\ -C(C_6H_5)CH_2Br \end{array}$$
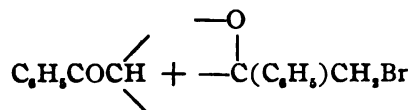
giving, by addition,[2] a glycid derivative,

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[1] Cf. Nef: Ann. Chem. (Liebig), **310**, 316; **335**, 252, 261.
[2] Cf. Nef: *Ibid.*, **335**, 272. Foot-note.

$$C_6H_5COCH\underset{\displaystyle O}{\triangle}C(C_6H_5)CH_2Br,$$
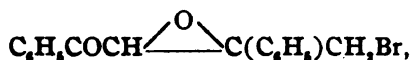
which can exist in two space isomeric modifications. Professor Nef informs me that he believes the recent work of Claisen[1] and Darzens[2] on the conversion of ketones and some aldehydes into glycid derivatives by means of chloracetic ether, in the presence of sodium ethylate or sodamide, can only be rationally interpreted on this basis,[3] *i. e.*, the methylenecarboxylate, present as a product of dissociation of chloracetic ether, simply unites with the various active ketone or aldehyde molecules present thus:

$$ROOCCH \diagdown \bigg/ \;+\; \overset{\displaystyle -O}{\underset{\displaystyle -CR.R'}{|}} \;\longrightarrow\; ROOCCH\underset{\displaystyle O}{\triangle}CR.R'.$$
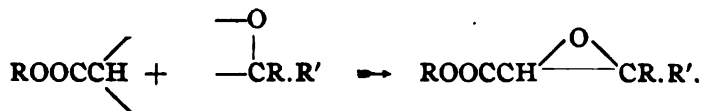
Interpretation II. cannot, however, possibly apply to the α- and β halogendiphenacyl derivatives under consideration, because there is absolutely nothing known in their behavior justifying the presence of a glycid group. Consequently, we are forced to turn back to interpretation I. On looking over the work of Paal and Schulze on α- and β-bromdiphenacyl, it is noteworthy that one finds there a great deal of evidence in favor of the new formulae given under I. for these compounds—as, for instance, the absence of hydroxyl groups, the impossibility of converting these compounds into the real γ-bromdiphenacyl and *vice versa*, or into dibenzoylethylene or furfuran derivatives.

The most striking observation, repeatedly made, is the fact that α- and β-bromdiphenacyl, on treatment with dry halogen hydrides, in acetic acid solution, at the ordinary temperature, give a strong odor of bromacetophenone! If the so-called α- and β-bromdiphenacyls have the constitution assigned to them

[1] Ber. d. chem. Ges., **38**, 693.

[2] Centrabl., 1905, I, p. 346.

[3] A similar interpretation obviously applies to the formation of the product

$$(CH_3)_2NC_6H_4N\underset{\displaystyle O}{\triangle}CHCH\underset{\displaystyle O}{\triangle}NC_6H_4N(CH_3)_2,$$

obtained recently by Torrey from *p*-nitrosodimethylaniline and ethylene bromide. Am. Chem. J., **34**, 475 (1905).

above under I. they, or their addition products, must be re-
solved, quantitatively, in the cold, by dry hydrogen bromide,
either into equal molecules of bromacetophenone and ω dibrom-
phenylmethylcarbinol, $C_6H_5CH(OH)CHBr_2$, or into 2 mols. of
bromacetophenone. I propose, therefore, to carry out experi-
ments in this direction at once. I have found, moreover, that
α- and β-bromdiphenacyls give, on treatment with fused sodium
acetate in acetic acid solution, at 100°, 66–68 per cent of the
theoretical amounts, viz., 2 mols. of benzoyl carbinol acetate
(see below). The isomeric α- and β-acetoxydiphenacyls, as
well as the β-oxydiphenacyl, also give a large yield of benzoyl
carbinol acetate on similar treatment. These results are self-
evident on the basis of the new formulæ for the compounds,
but cannot be understood on the basis of those of Paal and
Schulze. It should be remembered that the real, so-called
γ-bromdiphenacyl gives, quantitatively, on treatment with so-
dium acetate and acetic acid, trans-dibenzoylethylene. The only
observation which points in any way towards the old formulae
is the conversion of α- and β-bromdiphenacyl, by reduction with
zinc dust and alcohol, into diphenacyl. This experiment was,
therefore, repeated with the following result : Only a very
small amount, about 10 per cent, of diphenacyl and about an
equal quantity of acetophenone are formed. The main reac-
tion product is a non-volatile oil—probably α-phenacyloxy-
styrol, $CH_2 : C(C_6H_5)OCH_2COC_6H_5$, which at present is being
further investigated. The formation of small quantities of di-
phenacyl in the above experiment is not difficult to under-
stand on the basis of the new formulae ; one has only to remem-
ber that Claisen's analogous O-ethylacetophenone,[1]

$$CH_2 : C(C_6H_5)OC_2H_5,$$

undergoes rearrangement by heat (for the explanation, vide
Nef[2]) into C-ethylacetophenone, $C_6H_5COCH_2C_2H_5$. Further-
more, I have found that a mixture containing acetophenone
and bromacetophenone, when heated in a sealed tube at 100°,
with 10 per cent aqueous sodium hydroxide gives, among other

[1] Ber. d. chem. Ges., 29, 2931.
[2] Ann. Chem. (Liebig), 298, 372 ; 310, 316.

products, a very fair yield of diphenacyl—*i. e.*, an alkylation of acetophenone by benzoylmethylene[1] takes place. It is, therefore, exceedingly probable that the small amount of diphenacyl obtained by Paal and Fritz in their experiments was formed in some such manner.

Finally, I consider the existence of the fourth so-called δ-ioddiphenacyl of Paal and Schulze as extremely doubtful; I think that it consists simply of the pure β-isomer; as has been shown by Paal and Schulze, it certainly gives exactly the same reactions and derivatives as the so-called β-compound and possesses, practically, the same crystalline form.[2]

Although, in view of what has just been presented, I consider the formulae of Paal and Schulze as practically untenable, I still use, in the following experimental part, their nomenclature for the α- and β-substituted diphenacyl derivatives. It is my intention to continue the study of these derivatives and to include also a study of the corresponding compounds in the aliphatic series.

The Conversion of α- and β-Bromdiphenacyl into Two Molecules of Benzoyl Carbinol Acetate.—On treating bromacetophenone with 0.5 mol. of alcoholic sodium ethylate and allowing the mixture to stand at 0° for 2 days, I obtained about equal quantities of α- and β-bromdiphenacyl;[3] these were separated according to the directions of Paal, by means of cold benzene.

A solution of 1.55 grams (2 mols.) of fused sodium acetate, in 12 grams of glacial acetic acid, was cooled to 30°, 3 grams of β-bromdiphenacyl were added and the mixture heated for 6 hours, under a reversed condenser, in an oil-bath which was kept at 120°–130°. On pouring the dark red mixture into water, extracting with ether and washing with sodium carbonate solution, 3.10 grams of a dark brown oil were obtained. On distillation this gave 2.30 grams of pure benzoyl carbinol acetate, melting at 49°–50° and boiling at 160°–163° (18–20 mm.); this corresponds to 68 per cent of the theoretical amount. The

[1] Cf. Nef: Ann. Chem. (Liebig), 310, 316.
[2] Ber. d. chem. Ges., 36, 2411–2413.
[3] Cf. Fritz: *Ibid.*, 28, 3028. Also Paal and Demeler: *Ibid.*, 29, 2092.

product was further identified by its conversion by boiling water (*vide* Part I.) into benzoyl carbinol, melting at 86°.

A similar experiment with 3 grams of α-bromdiphenacyl, under practically the same conditions as in that just described, gave 0.50 gram of a reddish, non-volatile tar and 2.20 grams of pure benzoyl carbinol acetate, or 65.3 per cent of the theory.

The Conversion of α- and β-Acetoxydiphenacyl into Benzoyl Carbinol Acetate.—Paal and Schulze obtained β-acetoxydiphenacyl, melting at 98°, from the β-brom- or iodo-, as well as from the δ-ioddiphenacyl, on boiling with silver acetate and glacial acetic acid ;[1] this compound can be best obtained, as I have found, by heating a mixture of 4 grams of β-bromdiphenacyl, 3.82 grams of potassium acetate and 40 cc. of absolute alcohol, for 3 hours, in a sealed tube, at 100°. An odor of acetic ether was noticed on opening the tube, and, on adding water, extracting with ether and crystallizing from ether-ligroin, 2.65 grams of pure product, 71 per cent of the theory, were obtained. Two grams of this were heated in a bath, at 120°–130°, for 5 hours, with a solution of 1.04 grams of fused sodium acetate and 5 grams of glacial acetic acid. On working up as in the previous cases, 0.88 gram of non-volatile tar and 0.90 gram of pure benzoyl carbinol acetate, boiling at 153° (12 mm.) and melting at 49°–50°, were obtained ; this is 37 per cent of the theoretical amount.

According to Paal and Schulze, the α-bromdiphenacyl does not give the corresponding α-acetoxydiphenacyl on boiling with silver acetate and acetic acid ; two isomeric, high-melting compounds, $(C_8H_6O_4)_4$, which they call bisanhydrooxydiphenacyl, or tetrabenzoyltetramethylene, were obtained.[2] Such a compound, $(C_8H_6O_4)_4$, could, naturally, also be formed from the *cis*-ω-brom-α-phenacyloxystyrol,

$$BrCH$$

$$C_6H_5COCH_2OCC_6H_5,$$

by simple loss of hydrogen bromide, and this is the main reason for assigning the *cis*-formula to the α-bromdiphenacyl, as

[1] Ber. d chem. Ges., **36**, 2416.
[2] *Ibid.*, **36**, 2416.

above. I have, however, succeeded in obtaining totally different results by the action of alcoholic potassium acetate, 3.38 grams, on 3.75 grams of α-bromdiphenacyl, in a sealed tube, at 100°. Three and three-tenths grams of a thick, yellow oil were obtained, which I believe to be the crude α-acetoxydiphenacyl; it could not be obtained in a solid condition, but 2 grams of it, heated with sodium acetate and acetic acid, under exactly the same conditions as the β-acetate just described, gave 0.75 gram of non-distillable tar and 0.95 gram of pure distilled benzoyl carbinol acetate; this corresponds to 39.6 per cent of the theory.

β-Oxydiphenacyl.—On saponification of the β-acetoxydiphenacyl with alcoholic potassium hydroxide, Paal and Schulze obtained a yellow oil which, by treatment with sodium acetate and acetic anhydride, was converted back again into the original acetate; it must, therefore, have contained oxydiphenacyl. I have succeeded in obtaining β-oxydiphenacyl in the crystalline form; it is formed, besides an oily substance, not only from β-bromdiphenacyl, but also, probably by rearrangement into the β-space isomer, in smaller amounts (22 per cent yield) from α-bromdiphenacyl, by heating 2 grams of these compounds in 20 cc. of a methyl alcoholic solution of 1.5 mols. of potassium formate,[1] in sealed tubes, for 6 hours, at 100°. In the case of the β-isomer 0.95 gram of pure β-oxydiphenacyl was obtained, or 59 per cent of the theory; as the substance is very difficultly soluble in cold benzene and ether, it could readily be freed from a small amount, 0.65 gram, of the oily product. Crystallization from hot benzene gave microscopic needles of β-oxydiphenacyl, melting at 175°–178°. In the α-series 0.35 gram of the β-oxy compound and 1.25 grams of yellow oil were obtained. Analysis of the crystalline product:

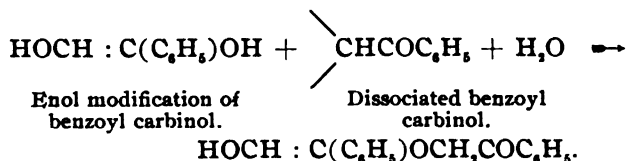0.1874 gram substance gave 0.5204 gram CO_2 and 0.0984 gram H_2O.

	Calculated for $C_{16}H_{14}O_3$.	Found.
C	75.59	75.72
H	5.51	5.83

[1] Nef: Ann. Chem. (Liebig), **335**, 260, 265.

A mixture of 1 gram of β-oxydiphenacyl, 0.64 gram of fused sodium acetate and 7.10 grams of glacial acetic acid, heated in an oil-bath, at 130°, for 6 hours, gave 0.40 gram of pure distilled benzoylcarbinol acetate and 0.30 gram of non-volatile tar. It should be emphasized, in this connection, that benzoyl carbinol itself, on heating under the same conditions with sodium acetate and acetic acid, remains entirely unchanged.

One and one-half grams of β-oxydiphenacyl, heated for 6 hours, at 130°, with 6 grams of acetic anhydride, gave 0.6 gram of β-acetoxydiphenacyl, melting at 98°–98°.5.

The question now arises whether any β-oxydiphenacyl is formed by the action of caustic alkalies on oxyacetophenone according to the equation,

$$HOCH : C(C_6H_5)OH + \diagdown CHCOC_6H_5 + H_2O \longrightarrow$$

<table>
<tr><td>Enol modification of
benzoyl carbinol.</td><td>Dissociated benzoyl
carbinol.</td></tr>
</table>

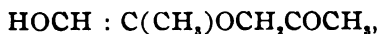$$HOCH : C(C_6H_5)OCH_2COC_6H_5.$$

I can simply state here that none was found; it is, however, exceedingly probable that a compound of this constitution must, under the conditions employed, take up water to form the isomeric aldehyde,

$$HCOCH(C_6H_5)OCH_2COC_6H_5,$$
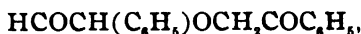
and this, by loss of water, can easily go over into a condensation product. Interpreted on this basis, the condensation product, $C_6H_8O_2$, obtained by Peratoner and Leonardi,[1] from acetol and aqueous barium hydroxide, must possess the constitution,

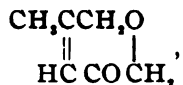$$\begin{matrix} CH_3CHOCH_2 \diagdown \\ | \quad\quad\quad\quad CO \; ; \\ CH : CH \diagup \end{matrix}$$
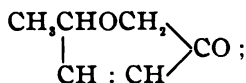
i. e., it must be 1-methyl-4-keto-Δ^2-dehydrohexone, being formed from β-acetonyl-α,β-dihydroxypropylene,

$$HOCH : C(CH_3)OCH_2COCH_3,$$

[1] Gazz. chim. ital., 30, 1, 577.

or the corresponding aldehyde, by loss of water. This corresponds, iu general, very closely to the formula,

$$CH_3CCH_2O$$
$$\|\qquad|$$
$$HC\ CO\ CH_2,$$

2-methyl-4-keto-Δ^2-dehydrohexone, assigned to it by Peratoner and Leonardi, and explains all the known reactions of the compound equally well. In view of this, I am encouraged to study still further the yellow tars obtained by the action of caustic alkalies on acetol and benzoyl carbinol, respectively.

On the Reduction of β-Bromdiphenacyl by Zinc Dust and Alcohol.—On treatment of β-bromdiphenacyl with these reagents, V. Fritz[1] obtained small quautitics of diphenacyl and acetophenone ; this observation was confirmed by Paal and Demeler,[2] who state that, in addition, a large amount of non-volatile oil is formed. I have repeated this experiment with 8 grams of material, 40 grams of zinc dust and 100 cc. of ethyl alcohol, heating 2.5 hours on a boiling water-bath. Five and one-tenth grams of crude reaction product were obtained on filtering, adding water and extracting with ether. The acetophenone was removed by heating in a bath up to 160° (18 mm.) ; only 0.5 gram was thus obtained and identified by conversion into the phenylhydrazone.[3] Three-tenths gram of diphenacyl, melting at 140°–142°, and converted into the characteristic dioxime,[4] melting at 202°, were obtained from the oil left on adding a small amount of alcohol and stirring. The remainder, 4.30 grams, and, therefore, the main reaction product, consisted of a thick, non-volatile oil, whose study is to be continued. It is, in all probability, α-phenacyloxystyrol,

$$CH_2 : C(C_6H_5)OCH_2COC_6H_5,$$
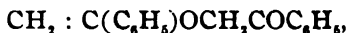
isomeric with diphenacyl and, therefore, formed by a direct reduction of β-bromdiphenacyl.

[1] Ber. d. chem. Ges., **28**, 3033.
[2] *Ibid.*, **29**, 2096.
[3] Bischler : *Ibid.*, **16**, 662.
[4] Paal and Kapf : *Ibid.*, **21**, 3057.

In conclusion, I wish to acknowledge my deep sense of gratitude to Professor Nef for his inspiring and careful guidance of this work.