No absorption of propene by cuprous chloride was observed after seventy-two hours at 11 atmospheres pressure and 23°.

The absorption of ethylene from a 60% ethylene–35% propene mixture was made by passing 22.3 liters of the mixture at 17.7 atmospheres pressure over 50 g. of cuprous chloride contained in a glass-lined pressure tube at a rate of 0.8 liter per hour. Four and one-half liters of absorbed gas was released from the cuprous chloride which contained no propene and 90% of ethylene. However, of the 13 liters of ethylene passed only 4 liters was absorbed, 0.35 mole for each mole of cuprous chloride.

Following a similar procedure, 0.2 liter of gas, which contained 70% of ethylene, was absorbed from 12.1 liters of a 61% ethylene–35% ethane mixture at 39 atmospheres pressure. In this case only 0.012 mole of ethylene was absorbed for each mole of cuprous chloride.

Summary

1. Ethylene under pressure gives an addition compound with solid cuprous chloride which contains one mole of ethylene for one mole of cuprous chloride, $CuCl \cdot C_2H_4$. The dissociation pressure of this addition compound varies from 2.14 atmospheres at 0° to 19.49 atmospheres at 40°. The addition compound decomposes completely at atmospheric pressure, slowly at 25° but rapidly at 100°.

2. Propene under pressure is not absorbed by solid cuprous chloride.

3. Ethylene in mixtures with ethane and propene was selectively absorbed and concentrated but the absorbed ethylene amounted to only 0.012 and 0.35 mole for each mole of cuprous chloride.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

Hydroxy Polyketones. I. The Alkylation of Benzoylformoin

BY A. H. BLATT

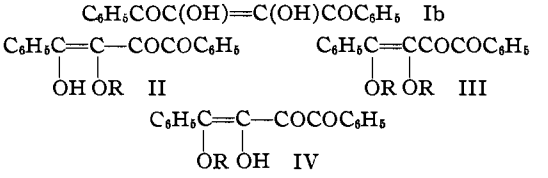
This article presents one part of what is planned as an extensive survey of the chemical behavior of the hydroxytriketone benzoylformoin (I), the benzoin of phenyl glyoxal, and of certain other structurally analogous substances.[1] Our interest in this group of compounds was occasioned in part by their unusual reactivity but, primarily, by the possibility of their existence as enols. For the enols of certain hydroxy polyketones would contain the ene-diol grouping characteristic of ascorbic acid and they should enable us to study, using synthetic material of definite structure and easy availability, the chemical behavior of the ene-diol system.

Benzoylformoin and a number of its analogs were first prepared and investigated by Söderbaum and by Abenius,[2] while the latter studied in detail the chemical behavior of benzoylformoin itself.[3] Abenius showed that benzoylformoin when dissolved in an alcohol and treated with hydrogen chloride formed a monoalkyl derivative and that a second alkyl group could be introduced into this monoalkylation product by means of an alcoholate and alkyl halide. The dialkyl derivatives on solution in sulfuric acid lost one alkyl group to form monoalkyl benzoylformoins isomeric with the monoalkylation products obtained from benzoylformoin itself. By using dialkyl derivatives containing two *different* alkyl groups Abenius showed that the alkyl group introduced by means of alcohol and acid was always the one eliminated by treatment with sulfuric acid. He also found that benzoylformoin and its first monoalkyl derivatives, in contrast to the dialkyl derivatives and the monoalkylation products derived from them, were oxidized by acid oxidants to diphenyl tetraketone. Abenius assigned to the monoalkyl derivatives obtained by the use of alcohol and acid the structure (II), to the dialkyl derivatives the structure (III), and to the second series of monoalkyl derivatives the structure (IV). Benzoylformoin, he considered

$C_6H_5COCHOHCOCOC_6H_5$ I

$C_6H_5C(OH)=C(OH)COCOC_6H_5$ Ia

$C_6H_5COC(OH)=C(OH)COC_6H_5$ Ib



(1) We are publishing certain of our results at this time because of the recent appearance of an article on formoins by Karrer and v. Segesser, *Helv. Chim. Acta*, **18**, 273 (1935).

(2) (a) Söderbaum, *Ber.*, **24**, 1381 (1891); (b) Abenius and Söderbaum, *ibid.*, p. 3034; (c) Söderbaum, *ibid.*, **25**, 3459 (1892); (d) Abenius and Söderbaum, *ibid.*, p. 3468.

(3) Abenius, (a) *Bihang Till K. Sv. Vet.-Akad. Handl.*, **20**, 3 (1894); (b) *Ber.*, **27**, 706 (1894).

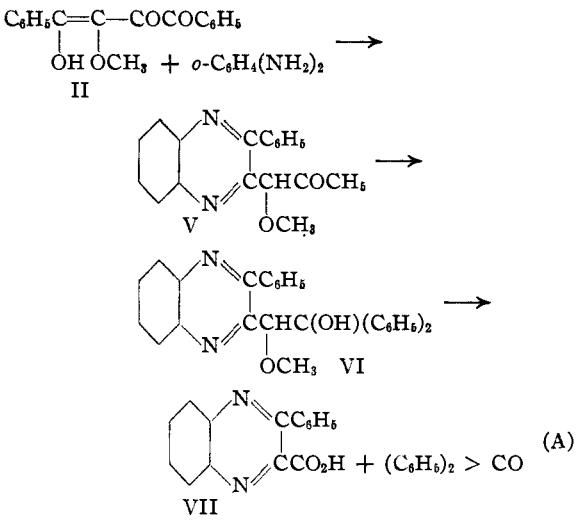
to be the hydroxy ketone (I) rather than the enol (Ia) from which the alkylation products are derived; the alternative enol (Ib) he eliminated from consideration because he was unable on the basis of this structure to account for two isomeric monoalkylation products.

We found it necessary to begin our work with the alkylation products of benzoylformoin for the striking differences in their behavior toward, for example, acids and acid oxidants are difficult to reconcile with the formulas assigned them by Abenius. A simple explanation for these differences in behavior would be available if the second alkyl group introduced were attached to carbon. Since Abenius offered no direct evidence on this point, we analyzed the dimethyl and diethyl benzoylformoins for alkoxyl and found that they were in fact dialkoxyl derivatives. With carbon alkylation eliminated, a more detailed study of the structures of the three alkyl derivatives was necessary and for this purpose we have examined their behavior toward various carbonyl reagents. With those reagents capable of reacting with the conjugated system C=C—C=O, the results were too complex to be of value but by using reagents specific for the carbonyl group we have been able to accumulate sufficient evidence to present definitive structures for the alkyl derivatives. Since the evidence for the structures of all the alkyl derivatives is quite closely interrelated and is primarily dependent on that for the second monomethyl derivative, it is best to begin our discussion with that second monomethyl derivative—the product formed from dimethyl benzoylformoin by loss of a methyl group.

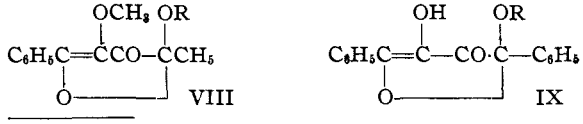
This methyl derivative reacts smoothly with *o*-phenylenediamine to form the quinoxaline (V), which on addition of phenylmagnesium bromide and subsequent oxidation furnishes benzophenone and 3-phenylquinoxaline-2-carboxylic acid (VII) —the reaction series (A).

These facts, coupled with the additional one that the methyl derivative is largely enolic in solution, serve to establish the structure of this second methyl derivative—hereafter to be referred to as the open chain methyl ether—as (II).

The open chain methyl ether (II) can be related to dimethyl benzoylformoin in several ways. Most illuminating is the conversion of the former into the latter by the use of methyl alcohol and hydrogen chloride. This type of etherification, characteristic of tertiary alcohols and glycosides,



suggests at once the cyclic structure (VIII, R = CH_3) for the dimethyl derivative. In agreement with this structure, and quite incompatible with the structure (III) assigned this same product by Abenius, is the chemical behavior of the material. It does not react with *o*-phenylenediamine nor with phenylhydrazine.[4] One alkyl group, the glycosidic group, can be removed by acid hydrolysis—that is to say, the formation of this glycosidic ether is reversible in an acid medium. If dimethyl benzoylformoin is dissolved in concentrated sulfuric acid and the solution poured onto ice, the open chain monomethyl ether (II) is formed. If dimethyl benzoylformoin is treated with ethyl alcohol and an acid the glycosidic methyl group is replaced by an ethyl group. If methyl ethyl benzoylformoin (VIII, R = C_2H_5), in which the ethyl group has been introduced by means of acid and ethyl alcohol and the methyl group by means of alcoholate and methyl iodide, is treated with methyl alcohol and acid, dimethyl benzoylformoin (VIII, R = CH_3) is formed. One reaction of dimethyl benzoylformoin is remarkable. In sodium methylate solution containing water the glycosidic methyl group is cleanly hydrolyzed, presumably as a result of ring opening, to form the open chain monomethyl ether (II). This alkaline hydrolysis is general for the glycosidic alkyl group in the various dialkyl benzoylformoins.



(4) Karrer and v. Segesser, Ref. 1, found that diethyl benzoylformoin does not react with *o*-phenylenediamine.

Finally, from the structures of the open chain methyl ether (II) and of dimethyl benzoylformoin (VIII) the structure of the first methyl derivative of benzoylformoin follows as the glycosidic ether (IX, $R=CH_3$). Its formation characterizes it as a glycoside and its behavior is also consistent with such a structure. It does not react with *o*-phenylenediamine nor with hydroxylamine hydrochloride. In acid solution one would expect, as in the case of dimethyl benzoylformoin, more or less complete reversal of the glycoside formation. With the dimethyl derivative it is easy to show that this reversal does take place using sulfuric acid for it leads to the open chain monomethyl ether which is comparatively stable in sulfuric acid. When the glycosidic monomethyl ether is dissolved in sulfuric acid it cannot be recovered but no definite products can be obtained. This result, however, is not surprising since benzoylformoin is destroyed by sulfuric acid but it is significant as indicating the hydrolysis of the glycosidic ether by acid. Definite evidence for the reversibility of the glycoside formation was obtained by establishing the occurrence of alkyl interchange in an acid medium. Thus when the methyl derivative (IX, $R=CH_3$) was treated with ethyl alcohol and an acid the ethyl derivative (IX, $R=C_2H_5$) was obtained. This ethyl derivative (IX, $R=C_2H_5$) on treatment with methyl alcohol and an acid furnished the methyl derivative (IX, $R=CH_3$). This reversal in acid solution of the glycoside formation accounts for the fact that the cyclic monoalkyl derivatives, alone of the three sets of alkylation products of benzoylformoin, are oxidized to diphenyl tetraketone by the same acid oxidizing agents which convert benzoylformoin to the tetraketone—the process consists of hydrolysis of the glycosidic ether to benzoylformoin and oxidation of the latter material.

We do not intend at this time to discuss the structure of benzoylformoin itself since this discussion will be more profitable after a full description of its behavior is available. It should be noted, however, that Karrer and v. Segesser have concluded from iodine titrations that benzoylformoin in solution is present as the ene-diol to the extent of 57%.

Experimental Part

Preparation of Benzoylformoin.—Certain modifications of the original procedure of Söderbaum[2a] are necessary in order to secure satisfactory and consistent results. Our preferred procedure is as follows. To 15 cc. of pure isonitrosoacetophenone, in a 50-cc. flask with a ground glass mouth, is added 15 g. of pure acetyl chloride. The flask is immediately connected to a reflux condenser (ground glass joint), plunged into an ice–water-bath and shaken until the reaction is complete. In a very few minutes the solid dissolves, then the reaction mixture quickly solidifies as a puff of hydrogen chloride is evolved. The solid cake is removed, pressed on a porous plate for five minutes, added to 400 cc. of water and stirred vigorously for fifteen minutes, then filtered. The solid (A) is dried and the filtrate made alkaline with half saturated sodium carbonate solution. The alkaline solution is filtered, acidified with cold dilute hydrochloric acid and the precipitated benzoylformoin is filtered and dried. The solid (A) is now stirred with an excess of half saturated sodium carbonate solution, filtered and the filtrate is acidified. The benzoylformoin secured at this point is combined with that obtained above, making a total yield of 8.5 to 9.5 g. or about 67%. The material is purified by dissolving 10 g. in 40 cc. of hot methanol containing 4 drops of 5% sodium hydroxide, to neutralize any acid present and prevent ether formation, filtering the solution and diluting it with 20 cc. of hot water. About 8.0 g. of pure benzoylformoin is obtained.

Benzoylformoin is a deep yellow solid which melts with decomposition to a dark red liquid at 187°. It is only moderately soluble in the ordinary organic solvents and insoluble in water. With sodium peroxide or alkaline hydrogen peroxide it furnishes two moles of benzoic acid. It dissolves in concentrated sulfuric acid to form an intensely colored brown solution which poured on water gives only an amorphous purple precipitate from which no definite products can be isolated. When attempts were made to alkylate benzoylformoin by means of diazomethane or alcoholate and alkyl halide no definite products could be isolated.

Preparation of the Cyclic Monomethyl Ether (IX, $R=CH_3$).—Dry hydrogen chloride was passed into a solution of 10.7 g. of benzoylformoin in 100 cc. of warm methanol until precipitation of the methyl ether began—about fifteen minutes. The reaction mixture was left in an ice chest overnight, then filtered from 9.7 g. of crude ether. The product was crystallized from 95 cc. of hot methanol and 20 cc. of water and furnished 9.0 g. of material melting at 182°. To the description of this ether given by Abenius[3a] (p. 20) we can add the following facts. The material contains one methoxyl group. (*Anal.* Calcd. for $C_{17}H_{14}O_4$: OCH_3, 11.00. Found: OCH_3, 11.06.) It does not react with *o*-phenylenediamine, and when it is dissolved in sulfuric acid it is converted into an amorphous purple product indistinguishable from that obtained from benzoylformoin by the same treatment. The methyl ether is not converted to an oxime by means of hydroxylamine hydrochloride with or without the addition of sodium acetate. When 1.0 g. of the methyl ether dissolved in 20 cc. of ethyl alcohol containing a small amount of sulfuric acid is warmed for ten minutes, then chilled, the product formed in excellent yield is the ethyl ether (IX, $R=C_2H_5$)[3b] (p. 712). Similarly, the ethyl ether (IX, $R=C_2H_5$) dissolved in methyl alcohol containing sulfuric acid and warmed for ten minutes furnishes the methyl ether (IX, $R=CH_3$).

Preparation of the Dimethyl Ether (VIII, R = CH_3).—To a solution of 8.4 g. of the cyclic monomethyl ether in 50 cc. of methanol containing 1.0 g. of sodium, an excess of methyl iodide was added and the solution was warmed for three hours, then left overnight. Water and ether were added and the ether extract on evaporation left 7.8 g. of the crude dimethyl derivative (87%). For analysis, the product was crystallized from methyl alcohol.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 73.0; H, 5.4; OCH_3, 20.95. Found: C, 73.1; H, 5.25; OCH_3, 20.88.

2,5-Diphenyl-3,5-dimethoxy-4-ketodihydrofuran (VIII) is a yellow solid moderately soluble in the ordinary solvents save petroleum ether. It melts at 78–79°. The ether reacts neither with phenylhydrazine nor with *o*-phenylenediamine. It is oxidized by neutral permanganate but the products are not significant. When it is warmed in ethyl alcohol solution containing sulfuric acid it is converted to methyl ethyl benzoylformoin (VIII, R = C_2H_5)[3b] (p. 718).

Preparation of the Open Chain Monomethyl Ether (II).—A solution of 8.9 g. of the dimethyl ether (VIII) in 35 cc. of methanol containing 1.6 g. of sodium was kept at the boiling point for ten minutes while 15 cc. of water was added. During this operation the original dichromate colored solution changed to a clear yellow and the addition of the last few cc. of water did not cause even a transitory precipitate. The solution was cooled, water and ether added, and the two layers separated. The water layer, after removal of the ether in an air stream, was acidified and furnished 7.4 g. of crude monomethyl ether (88%).

Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.3; H, 5.0; OCH_3, 11.0. Found, C, 71.7; H, 4.9; OCH_3, 11.0.

1,4-Diphenyl-1-hydroxy-2-methoxybutenedione (II) is a pale lemon-yellow solid which melts at 126–127°. It is very soluble in the ordinary solvents save petroleum ether and carbon tetrachloride and is best crystallized from the latter solvent. It reduces neutral permanganate very readily but the products are not particularly significant since we have found that one of the expected products, methyl benzoyl glyoxalate, is attacked by the reagent. Because of the color of its solutions an exact K. Meyer titration of the ether is not feasible. We were able, however, to show by indirect bromine titrations that in methyl alcohol the ether is at least 85% enolic and that it can be recovered after treatment with bromine, then potassium iodide and thiosulfate. The same ether can be prepared by solution of the dimethyl ether (VIII) in concentrated sulfuric acid followed by decompositon with ice but this preparation is erratic as the open chain methyl ether is to a considerable extent destroyed in the process.

In order to be certain that it is the glycosidic alkoxyl group which is removed by aqueous alcoholate we prepared the ethyl methyl ether (VIII, R = C_2H_5) by treating benzoylformoin with ethyl alcohol and hydrogen chloride and then methylating the product with sodium methylate and methyl iodide. This dialkyl benzoylformoin is converted into the open chain monomethyl ether (II) by sodium methylate solutions containing water just as is the dimethyl ether (VIII).

The monomethyl ether (II) in methyl alcoholic solution with dry hydrogen chloride is converted into the dimethyl ether (VIII, R = CH_3). The reaction is rapid and quantitative. Attempts to alkylate the monomethyl ether with alcoholate and alkyl halide gave no definite products.

Preparation of the Quinoxaline (V).—A solution of 2.8 g. of the monomethyl ether (II) and 1.5 g. of *o*-phenylenediamine in 15 cc. of hot methanol was boiled for forty-five minutes, then diluted with 10 cc. of hot water. On cooling, the dark red solution deposited 2.6 g. of the crude quinoxaline (73%). For analysis the product was crystallized from methanol and water. It was accompanied by small amounts of an orange impurity difficult to remove but when pure the quinoxaline was a straw colored solid melting at 131–132°, which was very soluble in acetone and acetic acid, sparingly soluble in benzene and insoluble in ether.

Anal. Calcd. for $C_{23}H_{18}O_2N_2$: C, 78.0; H, 5.1; OCH_3, 8.77. Found: C, 78.1; H, 5.2; OCH_3, 8.23.

Preparation and Oxidation of the Quinoxaline (VI).—The quinoxaline (V) dissolved in dry benzene was added to an excess of magnesium-free phenylmagnesium bromide. After thirty minutes of stirring the reaction was decomposed with iced dilute sulfuric acid and the highly colored product treated with methanol to remove the colored impurities. It was then purified by crystallization from methanol and obtained as a pale yellow solid, melting at 173–174°, very soluble in acetone and acetic acid and sparingly soluble in methanol.

Anal. Calcd. for $C_{29}H_{24}O_2N_2$: C, 80.55; H, 5.55; OCH_3, 7.2. Found: C, 80.5; H, 5.6; OCH_3, 7.37.

When the quinoxaline (VI) dissolved in acetic acid was oxidized with chromic oxide the reaction was strongly exothermic. The reaction mixture was shaken out with ether and the ether was extracted first with carbonate solution, then with sodium hydroxide and finally steam distilled. The steam distillation furnished benzophenone, the sodium carbonate extract furnished 3-phenylquinoxaline-2-carboxylic acid (VII),[5] and the sodium hydroxide extract furnished 2-hydroxy-3-phenylquinoxaline.[6] The identity of the products was established by mixed melting points with authentic specimens. The 2-hydroxy-3-phenylquinoxaline results, as we found by experiment, from the action of chromic oxide on the quinoxaline acid (VII).

Summary

It is shown that the alkylation of benzoylformoin with alcohol and an acid furnishes glycosidic ethers which can then undergo enolic alkylation by means of alcoholate and alkyl halide to form cyclic dialkoxyl derivatives. The dialkoxyl derivatives on treatment with alkali or acid lose the glycosidic alkyl group to furnish open chain monoalkyl derivatives of benzoylformoin.

WASHINGTON, D. C. RECEIVED APRIL 13, 1935

(5) Wahl, *Bull. soc. chim.*, [4] **1**, 461 (1907).

(6) Buraczewski and Marchlewski, *Ber.*, **34**, 4009 (1901).