

Summary

1. Boron or silicon fluoride dissolved in an alcohol forms with mercuric oxide a catalyst for acetylene reactions much superior to sulfuric acid.

2. Fluoboric and fluosilicic acids are probably the active constituents of these solutions, which have high electrical conductance and strong acid properties (Fig. 1).

3. Boron fluoride dissolved in ether to form $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$, b. p. 123° may also be used as a catalytic agent.

4. The catalysts are effective in very small quantities.

5. Using these catalysts, ethylidene ethers have been prepared from glycols, hydroxy acids and their derivatives by the acetylene method.

6. A number of these compounds have not previously been prepared and could not be made by any known methods from acetylene or from acetaldehyde.

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A STUDY OF THE DEHYDRATION OF DERIVATIVES OF ORTHO-BENZOYLBENZOIC ACID

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In a previous paper¹ it was stated that various methods for dehydrating *o*-benzoylbenzoic acid had been tried and that concentrated sulfuric acid appeared to be almost a specific for the conversion of this acid to anthraquinone. Velocity measurements gave a good constant at a variety of temperatures when values were substituted in the equation for a monomolecular reaction and the constancy was unaffected when the ratio of molecular concentrations was reduced to 13:1 (6:1 by weight), the lowest practical ratio.

The purpose of this work has been to compare the ease of formation of substituted anthraquinones from the corresponding substituted *o*-benzoylbenzoic acids. The method of carrying out the condensation was exactly the same as in the case of the unsubstituted acid, namely, equimolecular amounts of the reactants were dissolved in equal weights of concentrated sulfuric acid and the solutions were heated in a constant-temperature bath for a definite length of time.

Although a great variety of substituted *o*-benzoylbenzoic acids may be made by the Friedel-Crafts reaction, it was found that by no means all of them could be made to yield the corresponding anthraquinone, at least by the method which we used. In some cases traces of the anthraquinones were found but the yields were so small and the reaction product so com-

¹ Dougherty and Gleason, *THIS JOURNAL*, **51**, 310 (1929).

plex that analysis was impossible. Some of the compounds giving unsatisfactory results for one reason or another were as follows: 2'-hydroxy-4'-methylbenzoylbenzoic acid (m. p. 211°), mesityloylbenzoic acid (m. p. 212°), benzoylbenzamide (m. p. 162°), 4'-ethylbenzoylbenzoic acid (m. p. 126°), the propyl and butyl esters of *o*-benzoylbenzoic acid and benzophenone-*o,p'*-dicarboxylic acid (m. p. 235°). In the first two cases sulfonation of the acid occurred and there was no ring closure; in the third case there was no sulfonation but again no anthraquinone was formed; with the next three, small amounts of the anthraquinone were formed but the reaction product was a tarry mass and could not be worked. In the last case the anthraquinone was formed but the amount could not be determined by our method. Anthraquinones were obtained from neither *o*-benzoylbenzamide nor *o*-mesityloylbenzoic acid, although the condensation proceeds smoothly with *o*-benzoylbenzoyl chloride and with methyl *o*-benzoylbenzoate. The compounds giving the best results were the halogen and simple alkyl (methyl) derivatives. A list of these, with the percentage of the theoretical yield of the anthraquinone obtained, is given. The nomenclature used was based on the usual scheme of numbering the carbons in *o*-benzoylbenzoic acid.

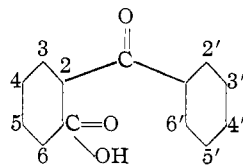


TABLE I
RESULTS OF EXPERIMENTS

No.	Benzoylbenzoic acid	Percentage of anthraquinone formed in hours			M. p. of product, °C.	
		3 at 75°	4 at 75°	4 at 105°		
2-		53.7	61.6		284	
1	4'-Chloro-2-			7.76	10.4	210
2	4'-Bromo-2-			9.3	11.8	205
3	4'-Methyl-2-	31.5	38.5			177
4	6(3)-Chloro-2-			46.6	59.0	162
5	2'-5'-Dichloro-2-				25.0	187.5
6	3,6-Dichloro-2-			21.0	27.0	187.5
7	3',4'-Dimethyl-2-	100	100			183
8	2',4'-Dimethyl-2-	78.2	83.7			161
9	2'(5')-Methyl-5'(2')-chloro-2-	82.8	85.0			164

It will be noted in a general way that the halogen has a retarding influence on ring closure (Nos. 1, 2, 4, 5 and 6); this is marked when the halogen is on either benzene ring and increases with the number of halogens present; the retarding influence is greatest when the halogen is on the ring which does not contain the carboxyl group. Bromine seems to have a slightly smaller effect than chlorine (Nos. 1 and 2) but the difference is so slight and so close to the limits of experimental error that no certain conclusions can be drawn.

The influence of the methyl group is not so consistent as in the case

of the halogen. One methyl group in Position 4', the only monomethyl compound which we could obtain easily, had a decidedly depressing effect on the ease of anthraquinone formation. When more than one methyl group was present, however, the reactivity was increased considerably above that of the unsubstituted *o*-benzoylbenzoic acid (Nos. 7 and 8). Of these two, No. 7, in which one of the methyl groups is para to the hydrogen atom which is eliminated in the reaction, shows the greater reactivity. This would be expected according to the general rules which govern substitution in the benzene ring. It might also be expected for the same reason that the chlorine atom in No. 1 and the methyl group in No. 3 would retard rather than accelerate anthraquinone formation. However, in such a complicated system as *o*-benzoylbenzoic acid, not much stress may be placed on the directing influence of groups obtaining in simple substitution reactions. For example, in No. 8 both methyl groups are meta to the hydrogen atom and yet this compound is more reactive than either No. 1, No. 2 or the unsubstituted *o*-benzoylbenzoic acid. By comparing No. 5 and No. 9, it can be seen that the retarding effect of chlorine is more than equaled by the accelerating effect of methyl when the two substituents are in the ring.

Mechanism of the Reaction.—When reaction velocity measurements were made using various substituted *o*-benzoylbenzoic acids, in no case was a constant for a monomolecular reaction obtained over any considerable period of the reaction time. The proposed mechanism in the case of the unsubstituted acid¹ involved a rapid reaction between *o*-benzoylbenzoic acid and sulfuric acid in which water was eliminated, and a much slower decomposition of the resulting compound, which was the step in the process actually measured. It would be quite apparent that if the two steps, in the case of the substituted acids, became of the same order of magnitude as regards velocity, it might be difficult to express the rate of the reaction in terms of any simple velocity equation. The water in this case would be eliminated at a measurable rate instead of very rapidly and there would be a progressive diminishing of the condensing power of the sulfuric acid. It seems probable that the failure to get results with the substituted acids comparable to those obtained when the unsubstituted compound was used may be accounted for in this way.

Experimental

The experimental procedure was much the same as that outlined in Part I,¹ with the single exception that it was frequently found necessary to dissolve the uncondensed benzoylbenzoic acids with dilute sodium carbonate, due to the fact that the sodium salts of the acids appeared to be much less soluble in the excess alkalinity of sodium hydroxide.

All of the substituted benzoylbenzoic acids were made by the Friedel-

Crafts synthesis using either the substituted phthalic anhydride and benzene or a substituted benzene and the anhydride. The resulting acids were recrystallized from various solvents until a high degree of purity was reached, *i. e.*, until the melting point agreed with that found in the literature, or until a sharp melting point was obtained in case it could not be found in the literature (Nos. 4 and 8). No serious difficulties were encountered due to the simultaneous formation of isomers.

Acids 1, 2 and 3 (m. p. 147.5, 172 and 140°, respectively) were prepared from phthalic anhydride and the monosubstituted benzene. No. 4 (m. p. 233.5°) was made from 3-chlorophthalic anhydride and benzene, the anhydride being prepared from the 3-nitro derivative as described by Bogert and Boroschek.² This compound could not be found in the literature so an analysis was made for chlorine: calcd., 13.62; found, 13.25. The high melting point of this acid seemed to indicate that it was the 6-chloro-2-benzoylbenzoic acid if analogy may be drawn from the fact that the 3-nitro-2-benzoylbenzoic acid has a melting point of 157–160° and the 6-nitro compound a melting point of 220–221°.³ No. 5 (m. p. 169°) was prepared according to the method of Phillips,⁴ although the yields were considerably below 27% of the theoretical which he obtained. No. 6 (m. p. 168.5°) was prepared from 3,6-dichlorophthalic anhydride and benzene; Nos. 7 and 8 (m. p. 161.5 and 143°) from phthalic anhydride and *o*- and *m*-xylene, respectively. No. 9 (m. p. 165°) was prepared from phthalic anhydride and *p*-chlorotoluene. Benzophenone-*o,p'*-dicarboxylic acid was made by oxidizing No. 3 with alkaline permanganate.⁵ The melting points of the product of each reaction are listed in the last column of the table and agree very closely with those given in the literature.

Summary

A number of substitution products of *o*-benzoylbenzoic acid have been synthesized, and attempts have been made to convert these into the corresponding anthraquinones. It was found that complete conversion took place in the case of the monohalogen and simple alkyl derivatives. A comparison was then made between the ease of ring closure of these derivatives and that of the unsubstituted acid.

Velocity measurements and constants indicated a fundamental difference between the mechanism of conversion of these acids and the unsubstituted acid, for which an explanation was offered.

A new compound, 6(3)-chloro-2-benzoylbenzoic acid, was prepared; melting point, 233.5°.

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² Bogert and Boroschek, *THIS JOURNAL*, **23**, 751 (1901).

³ Lawrence, *ibid.*, **42**, 1871 (1920).

⁴ Phillips, *ibid.*, **48**, 3198 (1926).

⁵ Limpricht, *Ann.*, **309**, 98 (1899).