The authors desire to acknowledge their indebtedness to the National Aniline and Chemical Company for the gift of a sample of their product.

## Summary

1. The dissociation of bromocresol green conforms to the theoretical formula over the useful portion of its alkaline range.

2. The apparent dissociation constant of a relatively pure sample of the indicator of laboratory origin was determined as 4.68. The values obtained with two commercial products were, respectively, 4.65 and 4.69.

WASHINGTON, D. C.

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

# THE REACTION BETWEEN METALLIC SODIUM AND AROMATIC ALDEHYDES, KETONES AND ESTERS. II. ESTERS

BY F. F. BLICKE

RECEIVED AUGUST 18, 1924 PUBLISHED JANUARY 8, 1925

In a previous paper[1] we have shown that benzaldehyde reacts with one or two atomic equivalents of metallic sodium to form highly colored, very reactive addition products. The study of these addition products is made difficult by the fact that during the formation of the aldehyde-sodium compounds a number of other products are also produced. The benzaldehyde disodium addition compound reacts with bromobenzene to form, among other substances, triphenylcarbinol.

Esters of aromatic acids react, likewise, with sodium to form deeply colored, very reactive addition compounds. Other investigators[2] have already noticed this phenomenon in the case of ethyl benzoate. The study of the reaction between ethyl benzoate and sodium by them, however, has been only of a preliminary nature, since it was not found possible to bring about complete reaction between the ester and the metal.

We have discovered in phenyl benzoate an ester especially suitable for the study of this reaction. When this ester, dissolved in absolute ether, is treated with one atomic equivalent of sodium at ordinary temperature a red-brown crust begins to form at once on the surface of the metal. This crust soon dissolves in the ether and leaves the metal with a bright, reactive surface. A flocculent precipitate also appears and increases in amount as the reaction progresses. It is essential that oxygen, carbon dioxide and moisture be excluded from contact with the reacting materials. After eight days the sodium completely disappears and a red-brown ether solution, which contains a considerable amount of the flocculent precipitate, is obtained.

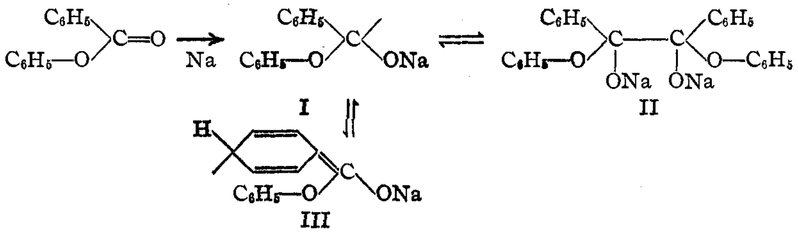
---

[1] Blicke, THIS JOURNAL, **46**, 2560 (1924).

[2] (a) Wahl, *Compt. rend.*, **147**, 73 (1908). (b) Scheibler and Voss, *Ber.*, **53**, 390, 392, 403 (1920). (c) Scheibler and Emden, *Ann.*, **434**, 268 (1923).

Concerning the reaction which takes place between the ester and one atomic equivalent of sodium we have formulated the following hypothesis. Esters, similarly to aldehydes and ketones, contain a carbonyl group; hence, the reaction between esters and sodium may be expected to take place in a manner analogous to the reaction which ensues when aldehydes or ketones[3] react with this metal.

The first phase of the reaction should then consist in the addition of sodium to the ester with the formation of a trivalent carbon compound (I). This substance not only resembles the ketone-sodium compounds but is also analogous to the triarylmethyls. Compound I, just like the ketone-sodium compounds and the triarylmethyls, may exist in equilibrium with a dimolecular form (II). Furthermore, the intense color of the ether solution may be best accounted for by the assumption of a colored, quinonoid form of the ester-sodium compound (III), just as has been done in the case of the triarylmethyls.[4]



The dimolecular form of ketone-sodium compounds is comparatively stable; the dimolecular form of the ester-sodium compound, however, is quite unstable and, in this instance, spontaneously loses sodium phenolate. The flocculent precipitate present in the reaction mixture represents this latter substance.[5] This was proved as follows. After mechanical separation of the precipitate from the reaction mixture and treatment of the former with dilute acid, phenol was obtained; this was isolated and identified in the form of tribromophenol. Furthermore, phenyl acetate was obtained upon the addition of acetyl chloride to the reaction mixture.

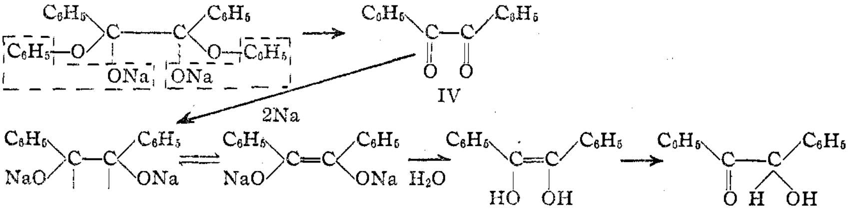
The elimination of sodium phenolate from the dimolecular form brings about its conversion into benzil (IV). Now, benzil itself reacts very readily with sodium in absolute ether and is thereby converted

---

[3] (a) Beckmann and Paul, *Ann.*, **266**, 6 (1891). (b) Schlenk and Weickel, *Ber.*, **44**, 1182 (1911). (c) Schlenk and Thal, *Ber.*, **46**, 2840 (1913). (d) Schlenk, Appenrodt, Michael and Thal, *Ber.*, **47**, 486 (1914).

[4] Gomberg and Cone, THIS JOURNAL, **39**, 3279 (1906). Gomberg and Sullivan, *ibid.*, **44**, 1810 (1922). Gomberg and Blicke, *ibid.*, **45**, 1765 (1923).

[5] Scheibler and Voss (Ref. 2 b, p. 393) have already suggested that in the case of the ethyl benzoate-sodium compound, sodium ethylate might possibly be spontaneously eliminated from the molecule.



IV

V VI VII

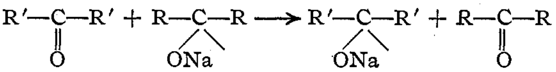
into a disodium addition product.[6] Staudinger and Binkert found that benzil, when treated with two atomic equivalents of potassium, forms first a blue-violet product, and upon further reaction of the substances a deep red-brown compound is produced. They regard the blue-violet substance as the potassium derivative of the unsaturated glycol, stilbene-diol, in quinhydrone-like combination with an equivalent amount of unchanged benzil. Further reaction of the quinhydrone compound with the metal converts all of the benzil into the red-brown dipotassium derivative of stilbene-diol; to the latter they assign a formula analogous to VI. The experiments of these investigators, as well as those of Nef,[6b] indicated that their view regarding the quinhydrone-like substance[7] is correct.

The acetyl,[6b] benzoyl[8] and methyl[9] derivatives of stilbene-diol, however, are all colorless substances and it is hardly possible that the potassium derivative, on the one hand, would be deeply colored while the esters and ethers, on the other hand, would be colorless. Now

---

[6] (a) Ref. 3 a, p. 23. (b) Nef, *Ann.*, **308**, 287 (1899). (c) Ref. 3 c, p. 2850. (d) Staudinger and Binkert, *Helvetica chim. Acta*, **5**, 705 (1922).

[7] The hypothesis of Staudinger and Binkert receives further confirmation from an experiment which has been carried out by Schlenk and Thal (Ref. 3 c, p. 2852). The latter investigators showed, first, that when a different ketone is added to a solution of a given ketone monopotassium (or sodium) addition product, the added ketone will often remove potassium from the original ketone-potassium compound with the result that a new metallic addition product is formed (Ref. 3 c, p. 2847):



$$\underset{\displaystyle O}{R'\!-\!\overset{\|}{C}\!-\!R'} + \underset{ONa}{R\!-\!C\!-\!R} \longrightarrow \underset{ONa}{R'\!-\!C\!-\!R'} + \underset{\displaystyle O}{R\!-\!\overset{\|}{C}\!-\!R}$$

When diphenyl ketene was added to the deep green solution of phenyl-biphenyl ketone-potassium a *red-violet* solution resulted. Upon the addition of more diphenyl ketene a light *brown* compound was precipitated. The latter substance, upon analysis, was found to consist of a combination of two molecular equivalents of diphenyl ketene with one atomic equivalent of potassium. The red-violet solution showed the characteristic behavior of a dissolved ketone monopotassium addition product and, undoubtedly, contained diphenyl ketene-potassium. The light brown compound must have been a quinhydrone-like combination, produced by union of the diphenyl ketene monopotassium and the added diphenyl ketene.

[8] Basse and Klinger, *Ber.*, **31**, 1217 (1898). Ref. 6 b.

[9] Ref. 6 d, p. 709.

it seems to us that when potassium or sodium reacts with benzil there must be formed first a trivalent carbon radical (V). This substance may then tautomerize to VI which we consider to be the metallic derivative of stilbene-diol—a *colorless* compound, or it may also tautomerize to a *colored*, quinoid modification of V and VI.

Upon the addition of water to the ester-sodium reaction mixture, and subsequent acidification of the aqueous layer, the following compounds were isolated: phenol, phenyl benzoate, a small amount of benzoic acid and an oil which was found to contain benzoin. The formation of phenol has already been accounted for. The origin of the phenyl benzoate can be accounted for in a number of ways: (1) the benzil formed during the reaction combines with a part of the sodium and, since only one atomic equivalent of metal was used, part of the ester must remain unchanged; (2) the ester is all converted into Compound I and the benzil formed then removes sodium from some of this compound with the formation of the benzil-sodium addition product and phenyl benzoate; (3) the ester unites with sodium phenolate, to some extent, to form an addition product—in the same manner that phenyl benzoate reacts with sodium ethylate[10]—and upon the addition of water this substance is resolved into its components; (4) phenyl benzoate and also benzaldehyde may result from an intramolecular oxidation and reduction which Compound I may undergo when the latter is treated with water. Such an oxidation and reduction of the ester-sodium compound would be analogous to that which has been established for the ketone-sodium compounds.[11]

That benzoin results from the decomposition of benzil-sodium (V or VI) by water has already been shown by others;[12] the unsaturated glycol (VII) is produced initially and this rearranges immediately into its stable form, benzoin.[13]

We were not able to determine whether or not the trivalent carbon radical (I) can be converted into a peroxide. Schlenk and Weickel[14] claim that the deep green dibiphenyl ketone monosodium compound is decolorized instantly by air and that sodium peroxide and dibiphenyl ketone are formed, due to the spontaneous decomposition of an unstable peroxide. A stream of air was passed into the phenyl

---

[10] Claisen, *Ber.*, **20**, 649 (1887).

[11] Ref. 3 b, p. 1187.

[12] Ref. 3 a, p. 24. Ref. 6 b. Ref. 6 d, p. 706.

[13] Nef (Ref. 6 b, p. 292) stated that he obtained benzoin from the action of sodium on ethyl benzoate and that the benzoin was formed through the intermediate production of a benzil-sodium compound; no experimental data are given by him. Wahl (Ref. 2 a) also obtained a small amount of benzoin by the addition of water to the ethyl benzoate-sodium product.

[14] Ref. 3 b, pp. 1184, 1186.

benzoate monosodium reaction mixture; decolorization did not result. Upon subsequent treatment of the reaction mixture with water the neutralized aqueous layer was found to react with acidified potassium iodide with the liberation of iodine. However, we failed to obtain the characteristic hydrogen peroxide tests with titanic sulfate or chromic acid and ether. It may be that the ester-sodium radical does not form a peroxide or, if it does form such a derivative, the latter may be more stable than the ketone-sodium analog.

Since the carbonyl group of aromatic ketones can be brought into reaction with two atomic equivalents of sodium,[3d] as well as with one, it might be expected that an analogous behavior would characterize the esters of aromatic acids. In the case of the ketones the reaction with two atomic equivalents of metal takes place, with the formation, of a monosodium addition product; this then absorbs a second equivalent of sodium with the production of a disodium addition product. This reaction proceeds smoothly since the ketone monosodium addition products, although very reactive chemically, are not subject to spontaneous decomposition.

We have no doubt regarding the formation of ester disodium compounds, although we were unable to obtain conclusive chemical evidence to support our view. Phenyl benzoate, for example, when dissolved in a mixture of ether and benzene reacts completely, but slowly, with two equivalents of sodium. This fact, however, does not prove that a disodium product had been formed; the monosodium compound which forms first is quickly converted, to some extent, into benzil which itself reacts readily with sodium. The reaction product, obtained from the interaction of phenyl benzoate with two equivalents of metal, consisted of a deep red-brown ether solution in which a considerable amount of a flocculent precipitate was suspended. Upon the addition of water to the mixture instant decolorization took place. As reaction products there were formed phenol, benzoic acid and traces of phenyl benzoate and benzoin. The amount of phenol obtained was practically equal to the amount which would result from the quantitative elimination of phenol from the ester. This result may indicate that the disodium addition product, similarly to the monosodium derivative, readily loses sodium phenolate from the molecule.

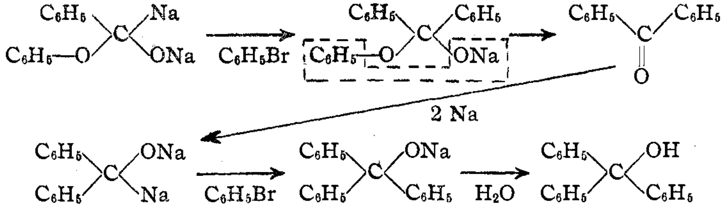
If phenyl benzoate and two equivalents of sodium are allowed to react in the presence of a third substance which will immediately react with the disodium product the instant it is formed, the resulting product will afford indirect evidence regarding the existence of phenyl benzoate disodium. This is illustrated by the following experiment.

Some years ago Acree[15] made this observation. When ethyl ben-

[15] Acree, *Am. Chem. J.*, **29**, 601 (1903).

zoate (1 mole), bromobenzene (2 moles) and metallic sodium (4 moles) are dissolved in absolute ether and allowed to remain in a sealed tube for 24 hours, at room temperature, the sodium all disappears and a deep blue precipitate is formed at the bottom of the tube. Upon addition of dilute acid to the reaction mixture triphenylcarbinol[16] is obtained together with smaller amounts of benzophenone, triphenylmethane and benzoic acid. We have repeated Acree's experiment with the use of phenyl instead of ethyl benzoate and found that, in this instance, triphenylcarbinol and phenol were the principal reaction products.

Nef[17] assumed that the triphenylcarbinol, in Acree's reaction, was produced through the intermediate formation of sodium phenyl. The following scheme however, in the case of phenyl benzoate, seems to offer a more rational explanation.



$$C_6H_5—CO—OC_6H_5 + 4\ Na + 2\ C_6H_5Br = (C_6H_5)_3C—ONa + C_6H_5—ONa + 2\ NaBr$$

Our explanation receives further support from the fact that Frey[18] found that benzophenone, bromobenzene (1 mole) and sodium (2 moles) react, in the presence of absolute ether, to give an almost quantitative yield of triphenylcarbinol.

The deep blue precipitate which Acree noticed was undoubtedly the insoluble sodium derivative of triphenylcarbinol, contaminated by traces of the blue benzophenone sodium derivative; the latter is quite insoluble in ether and, unless agitation of the reaction mixture is provided for, will react only partially with the bromobenzene.

We have also investigated the action of sodium on several other esters. Methyl benzoate reacts similarly to the ethyl homolog; a red-brown product is formed but in ether the reaction between the ester and the metal does not proceed to completion. Benzyl benzoate reacts with sodium, even more readily than the corresponding phenyl ester, to form a brown compound. In the case of phenyl $\alpha$-naphthoate a deep red reaction mixture is obtained. These reactions are described in detail in the experimental part of this paper.

---

[16] Schorigin [*Ber.*, **40**, 3115 (1907)] showed that ethyl benzoate, *iso*-amyl bromide and sodium react, in absolute ether, with the formation of phenyl-di-*iso*-amylcarbinol.

[17] Ref. 6 b, p. 291.

[18] Frey, *Ber.*, **28**, 2520 (1895).

Ethyl and phenyl hexahydrobenzoate were found to react very readily with sodium; colorless reaction products were formed. It must be mentioned, however, that the reaction of these two esters with sodium may be of a different type from that of the above-mentioned esters of aromatic acids. The esters of hexahydrobenzoic acid may react to form sodium derivatives of the enol form of the ester; in this event hydrogen would be produced. No pressure was ever observed in the reaction tubes, but this does not prove that hydrogen was not formed as a reaction product; it has been shown that the unsaturated ester enolates are reduced very readily.[19]

We found that the velocity of reaction varied considerably with the nature of the solvent used; in ether, or a mixture of ether and benzene the reactions took place most rapidly. Phenyl benzoate did not react with sodium when benzene was used as a solvent. Scheibler and Voss[20] have obtained some evidence which indicates that ester enolates, similar to Grignard compounds, may form addition products with ether. The speed of reaction must also depend upon the solubility of the various reaction products in the particular solvent.

It is possible that the catalytic action of ethyl acetate in certain reactions, in which sodium is one of the reacting materials, may be due to the formation of ester-sodium addition products. Of course, in the case of ethyl acetate the sodium derivative of the enol form of the ester may form in preference to a sodium addition product. The ethyl ester of trimethylacetic acid, which cannot enolize, reacts very readily with sodium. We are investigating the resulting product with regard to any possible catalytic action which it may possess. The investigation of the reaction between other esters and sodium is in progress.

## Experimental Part

**Reaction between Phenyl Benzoate and One Atomic Equivalent of Sodium.**—A test-tube containing 10 g. of pure phenyl benzoate was filled with dry nitrogen; after the addition of 1.2 g. of sodium, in the form of wire, the tube was constricted. Enough absolute ether was then added, usually about 50 cc., to fill the tube. The latter was sealed, wrapped in a black cloth to protect the mixture from light, and shaken at room temperature. Upon mixing the materials a red-brown crust began to form immediately upon the surface of the metal; when the tube was shaken the colored crust dissolved in the ether and left the metal with a clean, reactive surface. A flocculent precipitate also appeared and increased in amount as the reaction progressed. After the tube had been shaken for 24 hours about one-half of the metal seemed to have disappeared, and after seven to eight days the sodium had reacted completely, the tube contained a considerable amount of the flocculent precipitate and the ether was colored an intense brown-red.

REACTION WITH WATER.—About 40 cc. of distilled water was poured into a separatory funnel and a stream of nitrogen passed through it in order to remove dissolved air.

---

[19] Scheibler, Ziegner and Peffer, *Ber.*, **55**, 3923 (1922).

[20] Ref. 3 b, p. 393.

The contents of a tube, prepared as described above, were then poured into the funnel. The red-brown color of the reaction mixture disappeared at once upon contact of the latter with water. After the mixture had been shaken the aqueous layer was separated and more air-free water was added. This process was repeated several times and the ether layer was then separated and dried with fused sodium sulfate.

The combined aqueous layers were shaken with ether to remove any suspended matter; the aqueous layer was separated and a stream of air passed through it in order to remove the dissolved ether. A small amount of resinous material was usually obtained at this stage and was removed by filtration. Upon the addition of hydrochloric acid to the filtrate, benzoic acid was precipitated; this was separated by filtration. After recrystallization from petroleum ether the acid melted at 120–121°; mixed m. p., 121°. The filtrate, which smelled strongly of phenol, was diluted to 250 cc. Bromine water was added to 50 cc. of the solution; tribromophenol was precipitated. After recrystallization from alcohol it melted at 96°. The yield of tribromophenol from 250 cc. of solution was 9.5 g., which corresponds to 2.6 g. of phenol. If 10 g. of phenyl benzoate had been completely converted into Compound I, and if the latter had lost sodium phenolate quantitatively, 4.7 g. of phenol would have been formed.

The solvent was allowed to evaporate spontaneously from the ether layer; an oil intermixed with crystalline phenyl benzoate was obtained. Upon distillation of the mixture 3.2 g. of phenyl benzoate was obtained; mixed m. p., 67–68°. In another instance the oil was separated from the crystalline material by spreading the mixture on a porous plate. After some time the absorbed oil was extracted from the plate with ether. Upon evaporation of the solvent a gummy mass was obtained. The following experiments indicated that the gummy substance contained benzoin. The material reduced Fehling's solution and, upon the addition of alcoholic potassium hydroxide, it formed a deep red solution tinged with violet. When boiled with a 10% aqueous sodium hydroxide solution, in a current of air, benzilic acid was formed.[21] It was impossible to free the small amount of the latter substance from a certain amount of admixed benzoic acid. The mixture of the two acids, when treated with concd. sulfuric acid, yielded a purple-red solution; this is a characteristic test for benzilic acid. The yields of reaction products from six experiments were practically the same as recorded above.

REACTION WITH ACETYL CHLORIDE.—The reaction mixture, prepared from 20 g. of phenyl benzoate, was cooled with ice and then treated with 16 g. of acetyl chloride. A vigorous reaction took place and the red-brown mixture became light yellow. After 24 hours the mixture was poured onto ice. The residue obtained from the ether layer by removal of the solvent was distilled under diminished pressure. From the distillate there was obtained by fractional distillation 8.3 g. of phenyl acetate and 6.3 g. of phenyl benzoate. The phenyl acetate was identified by its boiling point and by its conversion, by hydrolysis, into phenol and acetic acid. The phenyl benzoate was identified by its melting point.

**Reaction between Phenyl Benzoate and Two Atomic Equivalents of Sodium.**—Ten g. of phenyl benzoate, 2.4 g. of sodium wire and about 50 cc. of solvent were shaken in a sealed tube. An equal mixture of ether and benzene seemed to be the best solvent for the preparation of the ester disodium compound. When ether alone was used the metal was attacked immediately, but a heavy red-brown crust soon formed on the surface of the sodium and prevented further reaction. When the ester was shaken with sodium in pure benzene a thin, colorless, protective layer formed on the metal, otherwise no reaction took place. In ether-benzene the reaction began very slowly but after some time proceeded fairly rapidly. After the mixture had been shaken for three weeks only traces of the metal remained unchanged. The reaction mixture, which consisted of a

---

[21] Klinger, *Ber.*, **19**, 1868 (1886).

deep red-brown ether solution in which a flocculent precipitate was suspended, was decomposed by water and treated in the usual manner. There was obtained 4.4 g. of phenol which was isolated in the form of tribromophenol; complete decomposition of the ester sodium product into sodium phenolate would result in the formation of 4.7 g. of phenol. In addition, 0.45 g. of benzoic acid and traces of phenyl benzoate and benzoin were found.

**Reaction between Ethyl and Phenyl Hexahydrobenzoate and One Atomic Equivalent of Sodium.**—The ethyl ester was prepared from 10 g. of hexahydrobenzoic acid and 100 cc. of absolute alcohol which had been partly saturated with hydrogen chloride.[22]

The phenyl ester, which is not described in the literature, was obtained in the following manner. Hexahydrobenzoic acid was converted into the acid chloride.[23] Sodium phenolate was then prepared by refluxing 6.2 g. of phenol, 1.5 g. of sodium and 50 cc. of absolute ether until all of the sodium had reacted; 10 g. of the acid chloride was added, in small amounts. After the mixture had been refluxed for two hours it was allowed to stand for some time, then poured into an evaporating dish and the solvent allowed to evaporate. The residue was washed with water and the ester dissolved in chloroform. The chloroform solution was dried with fused sodium sulfate, the solvent removed and the ester distilled under reduced pressure; it boiled at 160–163° (15 mm.); yield, 9.2 g. 1.000 g. of the material was refluxed for twelve hours with 2 g. of sodium hydroxide and 30 cc. of water; 0.42 g. of phenol, in the form of tribromophenol, was obtained; calculated amount, 0.46 g.

A mixture of 5.5 g. of the ethyl ester, 0.7 g. of sodium and 40 cc. of ether was put into a tube and the latter sealed. A reaction began at once and after $^1/_2$ hour a considerable amount of the metal had disappeared. After the mixture had been shaken for 12 hours all of the sodium had reacted and the tube contained a bulky, white precipitate. During the reaction a pale yellow-green color developed; this color we attribute to the presence of impurities in the ethyl ester rather than to the ester-sodium compound. Upon the addition of water to the reaction mixture there were obtained ethyl alcohol and an oil that boiled from 190° to 310°; the oil had the characteristic odor of ethyl hexahydrobenzoate. The ethyl alcohol was identified by its conversion into iodoform. Due to the extremely disagreeable and penetrating odor of hexahydrobenzoic acid and its esters this reaction was not investigated further.

Five g. of the phenyl ester, 0.56 g. of sodium and 40 cc. of ether were shaken in a sealed tube for 12 hours. A reaction began immediately upon mixing the substances and a white, flocculent precipitate was formed. At one time during the reaction a pale orange color developed but this soon disappeared. The colorless reaction mixture was poured into water. There were obtained 1.54 g. of phenol, which was isolated in the form of tribromophenol, and a colorless, sweet-smelling oil that possessed no definite boiling point.

**Benzyl Benzoate and Sodium.**—A mixture of 10.6 g. of benzyl benzoate, 1.2 g. of sodium (1 atomic equivalent) and 50 cc. of ether was shaken in a sealed tube. A red-brown crust began to form at once on the surface of the metal. After the tube had been shaken for 12 hours the sodium had practically all disappeared and the reaction mixture consisted of a brown ether solution in which a considerable amount of a flocculent precipitate was suspended. The mixture was shaken for 12 hours longer and then poured into oxygen-free water. The ether layer was washed with water several times and the aqueous layers were then combined and shaken with ether to remove any suspended matter. After the removal of dissolved ether by means of a stream of air the alkaline, aqueous layer was acidified with hydrochloric acid; 3.1 g. of a crystalline sub-

---

[22] Aschan, *Ann.*, **271**, 264 (1892).

[23] Meyer and Scharvin, *Ber.*, **30**, 1941 (1897).

stance was precipitated. This material proved to be benzoic acid; mixed m. p., 120–121°.

The solvent was removed from the ether layer and the residue distilled. The latter was found to consist of a mixture of compounds, and a greater quantity of material was necessary in order to effect a separation of these substances. The contents of five tubes were therefore mixed and decomposed with water as described above. The residue obtained from the ether layer was fractionally distilled. There were obtained benzyl alcohol, benzyl benzoate and a small amount of high-boiling liquid. The benzyl alcohol was identified by its boiling point and by the interaction of its sodium derivative with phthalyl chloride which resulted in the formation of the dibenzyl ester of phthalic acid;[24] m. p., 42–44°. Benzyl benzoate was identified through its hydrolytic products.

**Phenyl $\alpha$-Naphthoate and Sodium.**—The ester was prepared from 25.7 g. of $\alpha$-naphthoyl chloride,[25] 9.4 g. of phenol and 5 g. of sodium hydroxide, dissolved in 50 cc. of water. The acid chloride and phenol were mixed and the alkaline solution was then added, a few cc. at a time and vigorously stirred. The ester separated in solid form; it was washed with water and then recrystallized several times from alcohol; m. p., 98–99°.

Phenyl $\alpha$-naphthoate, dissolved in ether, reacts immediately with sodium with the formation of a red-brown crust on the surface of the metal. For the preparation of the sodium addition product, however, we found that ether diluted with benzene was more suitable than pure ether. The ester, sodium (1 atomic equivalent) and a mixture of equal amounts of ether and benzene were shaken in a sealed tube. During the first ten minutes no reaction seemed to take place but after the mixture had been shaken for two hours the solvent was colored a deep red. During the entire course of the reaction the metal retained a clean, reactive surface. After five days practically all of the sodium had reacted. The deep red solution was decomposed in the usual manner.

Upon acidification of the aqueous layer with hydrochloric acid 0.88 g. of a crystalline precipitate was obtained. This substance proved to be $\alpha$-naphthoic acid; mixed m. p., 160°. After removal of the naphthoic acid by filtration, the filtrate was treated with bromine water; 3.8 g. of tribromophenol, which corresponds to 1.06 g. of phenol, was obtained.

The solvent was allowed to evaporate spontaneously from the ether layer. A crystalline material, intermixed with a gummy substance, resulted. A portion of the crystalline substance was separated mechanically and washed with a small amount of cold benzene. The substance melted at 98–99° which proved it to be phenyl naphthoate. The gummy material reduced Fehling's solution and became a deep red upon the addition of alcoholic potassium hydroxide; these two reactions indicate the presence of a naphthyl analog of benzoin. It seems that the naphthalene derivatives analogous to the benzil series have not yet been prepared. It is our intention to attempt the preparation of these compounds.

**Reaction between Phenyl Benzoate, Bromobenzene and Sodium.**—The reaction was carried out in a long-necked flask which was fitted to a reflux condenser by means of a ground-glass connection. A T-tube was inserted in the top of the condenser; a stream of nitrogen was led into one arm of the tube while the other arm was closed with a soda-lime bulb.

After the apparatus had been filled with dry nitrogen 4.6 g. of sodium wire (4 atomic equivalents) and 150 cc. of absolute ether were placed in the flask; 10 g. of phenyl benzoate dissolved in 15.5 g. of bromobenzene (2 molecular equivalents), and a small amount of ether were then added. After a short time the ether became a deep red-brown and boiled vigorously. After 12 hours the reaction mixture consisted of a greenish-blue

---

[24] Meyer, *Ber.*, **28,** 1577 (1895).

[25] v. Braun, *Ber.*, **38,** 180 (1905).

ether layer and a deep blue, granular precipitate. The mixture was poured into ice water; instant decolorization took place and no unchanged sodium was noticed. The ether layer was separated and washed with water several times. The washings were then united with the alkaline, aqueous layer and treated as follows. Air was blown through the solution to remove dissolved ether and, after filtration from traces of resinous matter, the solution was diluted to 350 cc. Hydrochloric acid was added to a 100cc. portion and then bromine water. 4.85 g. of tribromophenol was precipitated.

The ether layer was dried with fused sodium sulfate and the solvent then removed by distillation. Upon cooling, most of the residue crystallized. A small amount of cold alcohol was added and the crystals were separated by filtration. After several recrystallizations from alcohol a portion of the material was mixed with triphenylcarbinol; mixed m. p., 161–162°; yield, 3.5 g. The solvent was allowed to evaporate spontaneously from the alcoholic filtrate and a further amount of carbinol was thus obtained (2.5 g.).

From 10 g. of the ester there were thus obtained 4.7 g. of phenol, in the form of tribromophenol (calcd. amount, 4.7 g.) and 6 g. of carbinol (calcd. amount, 13 g.).

## Summary

1. Esters of aromatic acids react with one atomic equivalent of metallic sodium at ordinary temperature, in the presence of absolute ether, with the formation of highly colored, very reactive addition products. In our opinion the colored products represent trivalent carbon radicals. These substances, similarly to the ketone sodium compounds and the triarylmethyls, may exist in a mono- or a dimolecular form. In the case of phenyl benzoate the dimolecular form of the radical loses sodium phenolate spontaneously with the formation of benzil; the benzil, in turn, reacts with sodium as has already been shown by other investigators.

Benzyl benzoate and phenyl $\alpha$-naphthoate behave similarly to phenyl benzoate. The ethyl and phenyl esters of hexahydrobenzoic acid react with sodium with the formation of colorless reaction products.

2. Phenyl benzoate also reacts with two equivalents of sodium. However, we have only been able to obtain indirect evidence regarding the existence of the ester disodium addition product.

3. Esters of benzoic acid react with bromobenzene and sodium in the presence of absolute ether with the formation of triphenylcarbinol. We have given a reaction mechanism which explains the formation of the carbinol.

ANN ARBOR, MICHIGAN