3-Hydroxy-3-phenylchroman (X)

A solution of 5 g. of 3-methoxy-3-phenylchroman (IX) in 25 cc. of dry benzene is shaken for five hours with 2.5 g. of acetyl chloride in 10 cc. of benzene. The solid left on evaporation of the benzene is treated with dil. sodium hydroxide solution, the liquid filtered and then acidified. The precipitate thus obtained is dried in a vacuum over phosphorus pentoxide for some time and then crystallized from chloroform from which it separates in small needles; m. p., 101–102°; yield, 71%. The addition of ferric chloride to a suspension in concd. sulfuric acid produces a violet coloration. 3-Hydroxy-3-phenylchroman (X) differs thus from 2-hydroxy-3-phenylchroman (V) which gives a reddish-violet coloration, and exactly the same color differences are observed in the case of acacatechin-tetramethyl ether [2-hydroxy-4,6,3′,4′-tetramethoxy-3-phenylchroman (I)] and isoacacatechin-tetramethyl ether [3-hydroxy-4,6,3′,4′-tetramethoxy-3-phenylchroman (II)].

Anal. Subs., 0.1500: CO_2, 0.4362; H_2O, 0.0862. Calc. for $C_{15}H_{14}O_2$: C, 79.6; H, 6.2. Found: C, 79.4; H, 6.4.

The ACETYL DERIVATIVE crystallizes from alcohol in small needles; m. p., 124–125°.

Anal. Subs., 0.1737: CO_2, 0.4853; H_2O, 0.0956. Calc. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0. Found: C, 76.2; H, 6.2.

In conclusion we wish to thank the Colston Research Society of the University of Bristol for a grant which has covered the expenses of this investigation.

Summary

2-Hydroxy-3-phenylchroman and 3-hydroxy-3-phenylchroman have been prepared by the same methods which had been used by Nierenstein for the syntheses of acacatechin-tetramethyl ether and isoacacatechin-tetramethyl ether.

BRISTOL, ENGLAND

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

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

BY F. F. BLICKE

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We became interested in this subject through the following incident. During the drying of solvent ether which had been used in the preparation of triphenylcarbinol a small quantity of a deep blue substance was formed. This material was observed after the impure ether had remained in contact with metallic sodium for several days at room temperature; the ether contained traces of methyl benzoate and bromobenzene. An investigation was then undertaken in order to determine what this blue precipitate was and how it was formed.

A preliminary experiment showed that sodium reacts readily with methyl benzoate, at room temperature, when the latter is dissolved in absolute ether. A red-brown crust soon appears on the surface of the metal and the formation of a flocculent precipitate is observed; as the colored crust dissolves in the ether the latter becomes deep red-brown. No evolution of hydrogen is noticed. The reaction must be carried out in the absence of oxygen, carbon dioxide and moisture.[1]

The formation of the blue substance mentioned above, which was subsequently found to result from the interaction of an ester-sodium compound and bromobenzene, will be taken up in the discussion of the reaction between esters and sodium.

Acree[2] reported that ethyl benzoate, sodium and bromobenzene react with the formation of triphenylcarbinol. Furthermore, Frey[3] found that benzaldehyde, sodium and bromobenzene also yield triphenylcarbinol. Benzophenone, likewise, is converted almost quantitatively into the same carbinol by interaction with sodium and bromobenzene.[3] These reactions were all carried out under identical conditions, namely, at room temperature with absolute ether as a solvent.

Now it seemed to us that in the formation of triphenylcarbinol from an ester, aldehyde or ketone—all carbonyl compounds—the same underlying reaction mechanism must apply in each case. According to our view, the initial phase of the reaction consists in the interaction of sodium with the ester, aldehyde or ketone with the formation of very reactive, colored addition products which contain *trivalent carbon;* these then react with the bromobenzene to form triphenylcarbinol. In order to test this hypothesis we decided to study in detail, first, the reaction between benzaldehyde and sodium and then the reaction of the aldehyde-sodium compounds with bromobenzene.

The fact that benzaldehyde reacts with sodium without the evolution of hydrogen has been known for a long time. Church[4] studied a green benzaldehyde-sodium addition product and reported that it was decomposed by water with the formation of equivalent amounts of benzyl alcohol

[1] Wahl [(a) *Compt. rend.*, **147**, 73 (1908)] and also Scheibler and co-workers [(b) *Ber.*, **53**, 390, 392, 403 (1920); (c) *Ann.*, **434**, 268 (1923)] found that ethyl benzoate reacts with sodium in the presence of absolute ether to form a reddish-brown product. They noticed, however, that although the sodium reacts quite rapidly at first, the reaction soon becomes sluggish and finally stops after only a fraction of the metal has reacted. Upon the addition of water to the product a small amount of benzoin was obtained. Potassium was found to react more vigorously with the ester, but the resulting compound soon turned black, which indicated decomposition. No further investigation of this subject was carried out by the above-mentioned investigators.

We have discovered that *phenyl* benzoate reacts rapidly and completely with sodium to form a highly colored product which does not decompose spontaneously. Details regarding this substance and its reactions will be published later.

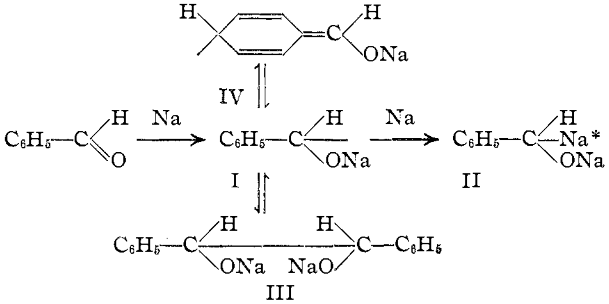
[2] Acree, *Am. Chem. J.*, **29**, 601 (1903).

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

[4] Church, *Ann.*, **128**, 295 (1863).

and benzaldehyde. Beckmann and Paul,[5] who seem to have been unaware of Church's work, next investigated the subject and found that the benzaldehyde-sodium compound was extremely sensitive toward water, oxygen and carbon dioxide; instant decolorization took place in the case of each reagent. In the interaction with water, hydrobenzoin (diphenyl glycol) and sodium hydroxide were the only reaction products found by them. The aldehyde-sodium compound is formed, according to the latter investigators, by the addition of one atomic equivalent of sodium to one molecular equivalent of aldehyde.[6]

We assume that benzaldehyde and sodium react with the formation of a mono- (I) or a disodium (II) addition product, depending upon the amount of sodium present. Compound I contains *trivalent carbon* and its behavior would be expected to be similar to that of the triarylmethyls. Accordingly, just like the latter substances, it will tend to polymerize to a dimolecular form (III) which probably exists in equilibrium[7] with the monomolecular compound.[8]



The green color of the aldehyde-monosodium compound is explained by the assumption of a quinonoid form IV. The existence of analogous quinonoid forms of trivalent carbon radicals, in tautomeric equilibrium with a colorless, benzenoid form has been demonstrated, in the case of the

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[5] Beckmann and Paul, *Ann.*, **266**, 25 (1891).

[6] Bernoulli and Schaaf [*Helv. chim. Acta*, **5**, 721 (1922)] recently described a green addition compound which they obtained by the interaction of benzaldehyde with metallic copper. The constitution of this substance was not determined but it is characterized by great chemical stability and hence has little, except color, in common with the unusually reactive benzaldehyde-sodium compounds.

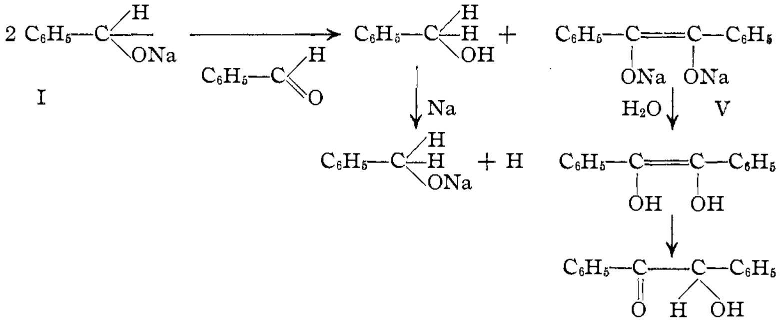
[7] Schlenk and Thal [*Ber.*, **46**, 2841 (1913)] showed that the disodium derivative of benzopinacol dissociates spontaneously, at ordinary temperature, into the benzophenone-monosodium compound; in other words, disodium benzopinacone is the dimolecular form of the benzophenone monosodium addition product.

[8] Nef [(a) *Ann.*, **308**, 286 (1899)] suggested Formula II but gave little or no experimental evidence to support his view. Formula III was proposed by Beckmann and Paul because it explains the formation of hydrobenzoin which they found resulted when the benzaldehyde-sodium compound was treated with water. This formula alone, however, is entirely inadequate in explaining all of the phenomena which are encountered in this reaction.

triarylmethyls, by Gomberg and Sullivan[9] and by Gomberg and Blicke.[10,11]

The experimental proof for the existence of Compounds I, II and III is furnished by the reactions which occur when water is added to the benzaldehyde-sodium compounds. Compound I is first hydrolyzed with the substitution of hydroxyl for ONa and the resulting substance then immediately undergoes intramolecular oxidation and reduction, just as Schlenk and Weickel[12] have shown in the case of the diaryl ketone-mono-sodium addition compounds; the resulting products, benzyl alcohol and benzaldehyde, were isolated. Compound II, upon the addition of water, is hydrolyzed into benzyl alcohol. In a similar manner Compound III undergoes hydrolysis with the formation of hydrobenzoin as Beckmann and Paul have already shown, but this compound we were unable to isolate. Compound IV is instantly transformed into the benzenoid modification by contact with water.

The above formulations represent the primary reactions between benzaldehyde and sodium. In reality, however, far more complex reactions take place due to secondary processes. For example, Compound I is an alcoholate and like other alcoholates can act as a reducing agent. It consequently interacts with benzaldehyde and reduces the latter to benzyl alcohol while Compound I, itself, is converted into Compound V.



The benzyl alcohol is acted upon by the sodium with the formation of sodium benzylate and hydrogen. It is very improbable that any hydrogen escapes from the reaction mixture; it will undoubtedly reduce either the

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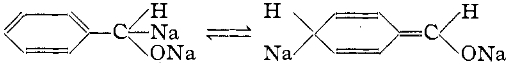
[9] Gomberg and Sullivan, This Journal, **44**, 1810 (1922).

[10] Gomberg and Blicke, *ibid.*, **45**, 1765 (1923).

[11] The color of the disodium compound of benzaldehyde (II) may be explained by the formulation of a quinonoid structure, similar to that used by Gomberg [Gomberg and Cone, *Ber.*, **39**, 2958 (1906); Gomberg, *Ber.*, **40**, 1874 (1907)] to explain the color of potassium triphenylmethane.



[12] Schlenk and Weickel, *Ber.*, **44**, 1187 (1911).

benzaldehyde or, more likely, the trivalent carbon radical. Upon the addition of water to the reaction mixture, Compound V is hydrolyzed to the unsaturated glycol which is unstable and rearranges at once into its stable form, benzoin.[13,14] Benzoin was detected by its characteristic tests and isolated in the form of benzilic acid.

Furthermore, Claisen[15] has shown that a small amount of sodium benzylate readily converts a large quantity of benzaldehyde into benzyl benzoate, the alcoholate being continually regenerated during the process. Accordingly, the sodium benzylate formed in the reaction will change some of the benzaldehyde into benzyl benzoate. We isolated this ester as a reaction product; but, as will be shown in a later paper, benzyl benzoate can also react with sodium to form colored products which undergo a complex series of changes. If no unchanged sodium is present in the reaction mixture at the time the ester is formed the latter will, of course, remain unchanged.

Finally, it has been shown[16] that benzyl ether and sodium benzoate are formed as by-products in the preparation of benzyl benzoate from sodium benzylate and benzaldehyde. We obtained sodium benzoate, in the form of benzoic acid, and an oil which was not hydrolyzed by refluxing it with aqueous sodium hydroxide. The oil boiled at the temperature given in the literature for benzyl ether.

The addition of one atomic equivalent of sodium to one molecular equivalent of benzaldehyde results, then, in the production of a mixture of compounds. A summation of the products formed by the addition of dilute acid to the reaction mixture, neglecting any products which might be formed from the interaction of benzyl benzoate and sodium, is as follows: benzyl alcohol (from Compound I, and from the interaction of I with benzaldehyde), benzaldehyde (from I), hydrobenzoin (from III), benzoin (from V), benzyl benzoate, benzyl ether and benzoic acid. We were able to isolate all of these products except hydrobenzoin.

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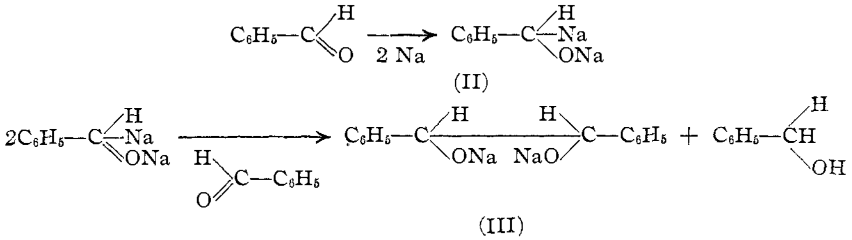
[13] Proof for this rearrangement is furnished by the experiments of a number of investigators. Ref. 8 a, p. 287. Bouveault and Locquin, *Compt. rend.*, **140**, 1593 (1905); *Bull. soc. chim.*, (3) **35**, 636 (1906). Scheifler and co-workers, Ref. 1 b, p. 388; *Ber.*, **55**, 789 (1922); *Z. angew. Chem.*, **35**, 321 (1922); Ref. 1 c, p. 265. Staudinger and Binkert, *Helvetica chim. Acta*, **5**, 703 (1922).

[14] Lachman [THIS JOURNAL, **46**, 716 (1924)] in a footnote stated that benzaldehyde and sodium yield benzoin. We had begun our investigation prior to the publication of Lachman's observation and discovered benzoin as a reaction product. Our hypothesis is entirely different from that with which Lachman was engaged; as mentioned above, our study of the reaction between benzaldehyde and sodium came about through an attempt to explain the formation of triphenylcarbinol from benzaldehyde, sodium and bromobenzene.

[15] (a) Claisen, *Ber.*, **20**, 649 (1887). Also (b) Kohn and Trantom, *J. Chem. Soc.*, **75**, 1161 (1899).

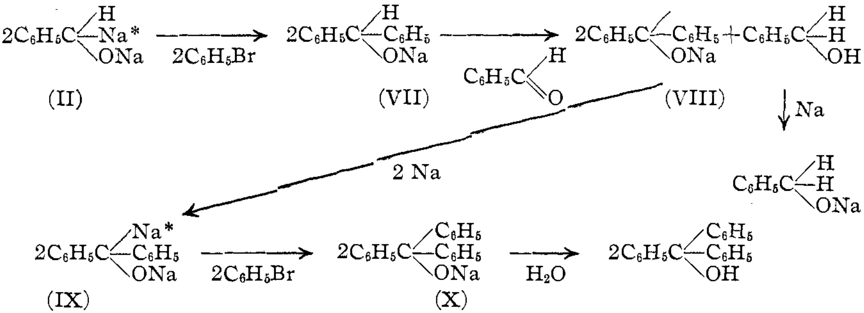
[16] O. Kamm and W. F. Kamm, *J. Am. Pharm. Assoc.*, 11, 599 (1922).

The reactions which take place when benzaldehyde reacts with two atomic equivalents of sodium are indicated below.



From the hydrolysis of Compound II we obtained benzyl alcohol and from III hydrobenzoin.

The formation of triphenylcarbinol from benzaldehyde, bromobenzene and sodium we explain as follows. The benzaldehyde-monosodium compound (I) is formed first and then the disodium derivative (II). In the latter one of the sodium atoms (Na*) is present in a very reactive form since it is bound directly to carbon and this sodium reacts with bromobenzene with the formation[17] of VII.



$$3C_6H_5CHO + 7Na + 4C_6H_5Br = 2(C_6H_5)_3C—ONa + C_6H_5CH_2ONa + 4NaBr + H$$

Now Compound VII contains two phenyl groups attached to carbon, but just how a third phenyl becomes linked to the same carbon with the formation of triphenylcarbinol is, at first, difficult to understand. However, when it is observed that VII, the sodium derivative of benzohydrol, is an alcoholate and that it may act as a reducing agent an explanation becomes apparent. It may be assumed that Compound VII reduces benzaldehyde to benzyl alcohol and that it, itself, is thereby oxidized to the trivalent carbon compound VIII; the latter is the monosodium compound of benzophenone and for this substance Formula VIII has been accepted.[18] From Schlenk's work we know that VIII readily absorbs sodium with

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[17] Schlenk, Appenrodt, Michael and Thal [*Ber.*, **47**, 487 (1914)] showed that, of the two sodium atoms present in phenyl-biphenyl ketone disodium, the sodium attached to carbon is far more reactive than the sodium attached to oxygen.

[18] Ref. 12, p. 1186.

the formation[19] of IX. Benzyl alcohol was isolated from the reaction mixture in an amount which, allowing for experimental error, checks well with that calculated. Furthermore, Compound VII was prepared from benzohydrol and sodium and allowed to react with benzaldehyde in ether solution. Benzyl alcohol was formed together with a small amount of the dimolecular form of VIII. The latter was isolated, not as benzopinacol, but in the form of its anhydride, α-benzopinacoline.[20]

The formation of the carbinol can now be readily understood. In Compound IX the reactive sodium (Na*) interacts with bromobenzene with the formation of the sodium derivative of triphenylcarbinol; the latter is instantly converted by water into triphenylcarbinol and sodium hydroxide.

It is the benzaldehyde-disodium compound which is responsible for the formation of triphenylcarbinol; the benzaldehyde-monosodium compound, however, must form before the disodium derivative. Now if the benzaldehyde-monosodium compound reacts as fast with benzaldehyde as it reacts with sodium, or if the monosodium compound is prevented from reacting with a second sodium by mechanical means such as would be caused by imperfect mixture of the components during the reaction, some or all of the products which have been mentioned under the reaction of benzaldehyde with one atomic equivalent of sodium will be formed. Similar reasoning, in the case of the benzaldehyde disodium compound, shows that some or all of the products formed when benzaldehyde reacts with two atomic equivalents of sodium may also be formed when benzaldehyde, sodium and bromobenzene are brought into reaction. The temperature and concentration of the reacting materials must also play an important role in the determination of the by-products which will be formed.

Substances in great variety are thus apt to result through the interaction of benzaldehyde, sodium and bromobenzene. The isolation of triphenylcarbinol from a considerable quantity of by-products was troublesome. In addition to the carbinol we were able to identify benzoin which resulted, no doubt, from the monosodium compound in the manner described, and α-benzopinacoline.

The benzaldehyde, sodium and bromobenzene may all be mixed at once and allowed to react, or the reaction between benzaldehyde and sodium, which results in the formation of the benzaldehyde-disodium compound,

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[19] VIII may also polymerize, to some extent, to the dimolecular form, the sodium derivative of benzopinacol. We did not find benzopinacol but a small amount of α-benzopinacoline was obtained as a reaction product.

[20] Sodium benzohydrolate may also be expected to react with benzaldehyde in a manner similar to that in which sodium methylate reacts with this aldehyde [Ref. 15 a]. In this instance there should then be formed benzohydrol, benzyl benzoate, benzyl alcohol and the benzohydrol ester of benzoic acid. We have obtained strong indications that this reaction does take place.

may be allowed to go to completion and the bromobenzene then be added; triphenylcarbinol and benzyl alcohol are obtained in both cases.

Nef[21] is the only one who has ever attempted to explain the fact that ethyl benzoate, benzaldehyde or benzophenone reacts with sodium and bromobenzene to form triphenylcarbinol. He assumed that sodium phenyl is formed and that this substance then reacts with the ester, aldehyde or ketone to form the carbinol. The following objections to Nef's view may be presented. If sodium phenyl and benzaldehyde react there should be formed diphenylcarbinol and not triphenylcarbinol; on the basis of formation of sodium phenyl how is the production of benzyl alcohol to be explained and how can the intense blue or green color of the reaction mixture be accounted[22] for? Acree[23] found that sodium phenyl reacts with bromobenzene instantly, even at the temperature of a freezing mixture, to form biphenyl. Considering, therefore, the great speed with which these two substances react it would seem that biphenyl should be one of the main reaction products when benzaldehyde, bromobenzene and sodium react with one another. In only one instance did we find any biphenyl and then the yield of this substance was very small (2 g. from 63 g. of bromobenzene).

To support further our view of the reaction mechanism described above we have discovered that when bromobenzene is replaced by *p*-bromotoluene or α-bromonaphthalene, benzyl alcohol is formed in each case in addition to the corresponding tertiary carbinol—diphenyltolylcarbinol and diphenyl-α-naphthyl carbinol.

Experimental Part

Reaction of Benzaldehyde with One Atomic Equivalent of 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. The apparatus was filled with dry nitrogen and a continuous stream of this gas was led over the top of the condenser during the reaction. The nitrogen exit tube was attached to a soda-lime bulb; in this manner the reaction mixture was protected from oxygen, carbon dioxide and moisture.

Forty-two g. of freshly distilled benzaldehyde and 9.2 g. of sodium in the form of wire were brought into reaction in 150 cc. of absolute ether. The sodium was added in five portions during two-hour intervals, and more ether was added if the reaction mixture became too pasty. Upon addition of the first portion of metal a colorless, flocculent precipitate gradually formed; the latter resulted from the decomposition of the colored reaction product by traces of oxygen and moisture present in the apparatus. Later a brownish-green material formed and finally the intense green precipitate, the benzaldehyde-monosodium compound, made its appearance. When the sodium is added all in one portion a very vigorous reaction results and the green product is formed

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[21] Ref. 8 a, p. 291.

[22] Acree, [Ref. 2, p. 590] reported that sodium phenyl is a light brown compound.

[23] Ref. 2, p. 593.

at once. The reaction was allowed to proceed at room temperature and the mixture was shaken frequently. After 48 hours the material was poured into 24 g. of acetic acid and 60 g. of ice while the mixture was vigorously stirred. In order to protect the benzaldehyde, which is formed as a reaction product, and the extremely sensitive aldehyde-sodium compound from oxidation by air the decomposition with dilute acid was carried out in a flask filled with nitrogen. The acetic acid neutralized the alkali, which would otherwise be formed, and prevented even to any slight extent conversion of benzaldehyde into benzyl alcohol and benzoic acid.[24] The ether layer was separated, dried with fused sodium sulfate and the ether then removed by distillation. The residue was distilled and separated into three fractions boiling at 150–235°, 235–295° and 295–330°, respectively. A gummy residue was obtained in the distilling flask. The lower-boiling fraction, which smelled strongly of benzaldehyde, contained most of the benzyl alcohol. The latter was freed from benzaldehyde by conversion of the aldehyde into benzoic acid by oxidation with air; the acid was then extracted with sodium carbonate solution. The benzyl alcohol was identified by its boiling point and by allowing it to react with phthalic chloride whereby the dibenzyl ester of phthalic acid was formed; the ester melted at 42–43° as recorded in the literature.[25] Benzoic acid separated in crystalline form from the middle-boiling portion. The highest-boiling fraction consisted of a small amount of benzoic acid, benzyl ether and benzyl benzoate. The two last mentioned products were identified as follows. A portion of the mixture was dissolved in ether, the ether solution shaken with aqueous sodium carbonate to extract the benzoic acid and the ether layer separated. The ether was evaporated and the oily residue was refluxed with dil. sodium hydroxide solution for 12 hours; a control experiment with an equal portion of pure benzyl benzoate showed that this ester, under the same conditions, was completely hydrolyzed in ten hours. The undissolved oil was extracted with ether, the ether distilled and the residue fractionated. Benzyl alcohol and an oil that boiled at the temperature given in the literature for benzyl ether were obtained. Upon acidification of the alkaline layer benzoic acid was precipitated.

We were not able to free completely from admixed impurities the benzoin obtained from the gummy residue, however, the material obtained gave the typical benzoin tests: it reduced Fehling's solution and yielded a violet solution with alcoholic potassium hydroxide. Upon boiling it with aqueous sodium hydroxide in a current of air, benzilic acid[26] was obtained and isolated in pure form. After recrystallization it melted, mixed with benzilic acid which had been prepared from benzil, at 148–150°. The acid also gave the characteristic purple solution with concd. sulfuric acid.

To convert a given amount of benzaldehyde quantitatively into the monosodium addition product seems impossible because of the unavoidable secondary reactions which take place. It is, moreover, difficult to convert even a major portion of the benzaldehyde into the addition product for the following reasons. When all of the sodium is added to the benzaldehyde at once the metal remains bright and reactive at first but toward the end of the reaction it becomes encrusted with the insoluble reaction product and consequently a portion of the metal remains unacted upon. In an attempt to eliminate this objectionable feature the sodium was added in portions at two-hour intervals. This procedure, however, was not entirely satisfactory, as it resulted in an increase in the yield of one of the by-products, the benzyl benzoate; this is due to the fact that the sodium benzylate which forms with the first addition of the sodium, rapidly converts benzaldehyde into benzyl benzoate as Claisen has shown.[15a] As a result, a part of the benzaldehyde is made unavailable for the formation of the sodium addition product.

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[24] Meyer, *Ber.*, 14, 2390 (1881). Ref. 15 b, p. 1158.

[25] Meyer and Jugilewitsch, *Ber.*, **30**, 780 (1897).

[26] Klinger, *Ber.*, **19**, 1868 (1886). Knoevenagel and Arndts, *Ber.*, **35**, 1982 (1902).

That the sodium benzylate formed in the reaction actually has the above-mentioned effect was shown by the following experiment. The reaction between one atomic equivalent of sodium and benzaldehyde was allowed to go to completion and another molecular equivalent of benzaldehyde was then added. A vigorous reaction took place and, judging from the yield of benzyl benzoate obtained, most of the added benzaldehyde must have been converted into this ester.

Reaction of Benzaldehyde with Two Atomic Equivalents of Sodium.—This reaction was carried out in the same manner as described under the reaction with one equivalent of sodium except that mechanical stirring was introduced. Eighteen g. of sodium wire was added to 42 g. of benzaldehyde dissolved in 150 cc. of absolute ether. After the mixture has been stirred continuously for eight hours it was found that no unchanged benzaldehyde remained in the flask. The deep green, insoluble addition product was washed free from unchanged sodium with ether and poured into 50 g. of acetic acid and 150 g. of ice. The ether layer was separated and the solvent removed by distillation. Upon fractionation of the residue there were obtained benzyl alcohol and a crystalline solid which, after repeated recrystallization from alcohol, was found to melt at 134°. When this material was mixed with hydrobenzoin, prepared from the reduction of benzoin,[27] the melting point remained unchanged.

The Reaction between Benzaldehyde, Sodium and Bromobenzene.—Twenty-one g. (7 atomic equivalents) of sodium in the form of wire and 150 cc. of absolute ether were placed in the apparatus used for the preparation of the aldehyde-sodium compounds and 42 g. of freshly distilled benzaldehyde was added. A vigorous reaction, which necessitated cooling, began almost immediately. The sodium became covered with a red-brown crust which quickly dissolved in the ether and left the metal with a bright surface. A green tinge then began to appear in the reaction mixture and after ten minutes 83 g. (4 molecular equivalents) of bromobenzene was added. The mixture was shaken frequently. After the reaction had progressed for 45 minutes a deep blue precipitate was noticed in the flask and this gradually turned into a very dark green, granular substance. The reaction became less vigorous after four hours, and after twenty hours longer at room temperature it seemed to have gone to completion. The reaction mixture was then poured, a little at a time, into a vigorously stirred mixture of 55 g. of acetic acid and 100 g. of ice. The intense color of the mixture was instantly destroyed by contact with the dil. acid. Only traces of unchanged sodium were noticed. The ether layer was separated and the solvent allowed to evaporate spontaneously. The residue consisted of crystals and an oil. The mixture was then poured into a Claisen flask and distilled under 15 mm. pressure. When the bath in which the distilling flask was immersed had reached the temperature of 190° the distillation was stopped. Upon fractionation of the distillate under atmospheric pressure benzyl alcohol, which boiled from 200–206° was obtained. The yield varied in different instances from 9 to 12 g.; calculated yield, 14 g. In addition to the determination of the boiling point the benzyl alcohol was further identified as follows. A portion was dissolved in ether and a current of air was passed into the solution to oxidize any traces of benzaldehyde which might have been present. The ether solution was then treated with aqueous sodium carbonate, the ether layer separated, dried, and the solvent removed by distillation. The benzyl alcohol was then converted into benzaldehyde and the latter identified through conversion into its phenylhydrazone; m. p.,[28] 156°.

The residue in the distilling flask was dissolved in the smallest possible amount of hot alcohol. After several days 8 g. of crystalline material had separated from the

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[27] Apitzsch and Metzger, *Ber.*, **37**, 1677 (1904).

[28] Mulliken, "The Identification of Pure Organic Compounds," John Wiley and Sons, **1914**, Vol. 1, p. 167.

alcoholic solution. The crystals were separated by filtration; a mixed melting point (160–161°) showed that the substance was triphenyl carbinol. The filtrate reduced Fehling's solution and gave a red-violet color upon the addition of alcoholic potassium hydroxide. These reactions indicated the presence of benzoin, although we were not able to isolate the latter substance in crystalline form. It was obtained, however, in the form of an oxidation product, namely, benzilic acid. A portion of the filtrate was refluxed for seven hours with 10% aqueous sodium hydroxide. During this operation a stream of air was passed through the mixture. The alcohol was then evaporated on a steam-bath and the oily layer separated from the alkaline solution. The latter was shaken with ether to remove suspended matter. After air had been blown through the alkaline layer to remove dissolved ether, it was acidified with hydrochloric acid. The precipitated acid was recrystallized several times from water; m. p. 150°. The benzilic acid gave the characteristic purple solution when treated with concd. sulfuric acid.

Benzaldehyde, Sodium and *p*-Bromotoluene.—Sixteen g. of sodium, 120 cc. of absolute ether and 32 g. of benzaldehyde were mixed in a flask; the same precautions were used as in preceding experiments. After the sodium and aldehyde had reacted for several minutes, 68 g. of *p*-bromotoluene was added. A vigorous reaction took place and it was necessary to cool the reaction mixture with ice. After about an hour the mixture was allowed to remain at room temperature. The reaction seemed to be complete after 24 hours. The contents of the flask were then poured into 42 g. of acetic acid and 100 g. of ice. The ether layer was separated and the oil, obtained from removal of the ether by distillation, was subjected to distillation under 15 mm. pressure. After the temperature of the bath in which the distilling flask was immersed, had risen to 180° the distillation was stopped. From the distillate there was obtained 8 g. of benzyl alcohol (calculated amount, 10.7 g.) and a mixture of other liquid products which boiled from 220° to 340°. All attempts to obtain diphenyl-*p*-tolyl carbinol in crystalline form from the sirupy residue in the distilling flask were unsuccessful. The carbinol was finally isolated in the form of its oxidation product, *p*-carboxylic-triphenyl carbinol. This was accomplished in the following manner: 12 g. of the sirupy mass, 48 g. of potassium dichromate, 72 g. of sulfuric acid and 100 cc. of water were boiled for five hours. The reaction mixture was allowed to cool and the liquid decanted from the solid matter. After the latter had been washed with water it was extracted with hot 3% sodium hydroxide. Upon acidification of the alkaline solution a crystalline acid was obtained. This was boiled with water several times to remove a small amount of benzoic acid and then dried. After several recrystallizations from benzene the substance melted[29] at 198–200°.

Benzaldehyde, Sodium and Alpha-Bromonaphthalene.—Thirty-two g. of benzaldehyde, 16 g. of sodium and 82.8 g. of bromonaphthalene were brought into reaction, the usual precautions being observed. After 36 hours the reaction mixture was treated as in the preceding cases with the exception that the residue obtained from the ether layer was distilled with steam instead of in a vacuum. After saturation of the aqueous distillate with potassium carbonate there were obtained 6.5 g. of benzyl alcohol and 22 g. of crystalline material which boiled from 208–240°; the latter consisted principally of naphthalene.

The oily residue from the steam distillation could not be crystallized and it was consequently impossible to obtain diphenyl-α-naphthyl carbinol itself. The latter substance, however, was isolated in the form of its characteristic derivative, phenyl-chrysofluorene.[30] In order to prepare the fluorene the oily material was first refluxed for

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[29] Hemilian, *Ber.*, **7**, 1201 (1874). O. Fischer and Albert, *Ber.*, **26**, 3081 (1893). Bistrzycki and Gyr, *Ber.*, **37**, 657 (1904).

[30] Ullmann and Mourawiew-Winigrodoff, *Ber.*, **38**, 2215 (1905).

several hours with dil. sodium hydroxide in order to remove all hydrolyzable material. The substance was then dissolved in hot glacial acetic acid. After the addition of a few drops of hydrochloric acid the solution was boiled for a short time and then allowed to cool. A small amount of the fluorene precipitated and this was found to melt at 194–195°.

Summary

1. One molecular equivalent of benzaldehyde reacts vigorously with one atomic equivalent of sodium with the formation of a colored, very reactive addition product which we consider to contain trivalent carbon. In addition, there result a number of by-products, the formation of which it is impossible to prevent. These by-products, some of which are present in the form of their sodium derivatives, were found to be benzyl alcohol, benzoin, benzyl benzoate, benzyl ether and benzoic acid; we were unable to isolate hydrobenzoin, which is probably also formed. We have given what seems to us to be a rational explanation for the formation of all of these products.

2. One molecular equivalent of benzaldehyde reacts with two atomic equivalents of sodium with the formation of a colored disodium addition product; benzyl alcohol and hydrobenzoin, in the form of their sodium derivatives, are also formed.

3. Benzaldehyde, sodium and bromobenzene react with the formation of triphenyl carbinol. Simultaneously there result, among other products, benzyl alcohol and benzoin. We have proposed a reaction mechanism which explains the formation of these products.

4. According to our hypothesis benzyl alcohol must be formed as a by-product when benzaldehyde and sodium react with an aryl halide with the formation of a tertiary carbinol. In conformity with this assumption it was found that benzaldehyde, sodium and *p*-tolyl bromide yield benzyl alcohol and diphenyl-*p*-tolyl carbinol; when α-naphthyl bromide was used benzyl alcohol and diphenyl-α-naphthyl carbinol resulted.

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