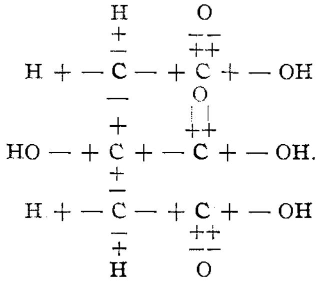

CHICAGO, ILLINOIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE REACTION BETWEEN ACID HALIDES AND ALDEHYDES. I.

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Although the addition and condensation reactions of aldehydes and ketones have been widely investigated, it is a surprising fact that their action with acid halides has received comparatively little attention. In only one or two of the largest amd most extensive text-books on organic chemistry is this reaction even mentioned. An investigation was therefore started in this laboratory to ascertain whether or not the reaction between aldehydes and acid halides is a general one in the aliphatic as well as aromatic series, and to determine the structure, properties and reactions of the resulting compounds. From the results so far attained, the indications are that the reaction is indeed a general one.

In this paper are given (1) a description of a number of the addition compounds prepared by the action of benzaldehyde and certain substituted benzaldehydes on various aromatic acid chlorides and bromides; (2) a description of a series of addition compounds of oxalyl bromide and aromatic aldehydes; (3) the proof of the structure of these compounds as shown by a study of the substance produced from benzaldehyde and benzoyl bromide; (4) a description of the preliminary study of the reactions of these compounds with various reagents.

A brief review of what already has appeared in the literature concerning these compounds is as follows: Wurtz[1] obtained a compound by the action of chlorine on acetaldehyde which Simpson[2] and Franchimont[3] proved to be the same as that obtained by the action of acetyl chloride on acetaldehyde, and which Schiff[4] later showed to have the structure of the addition compound $CH_3CHClOCOCH_3$. A number of similar addition compounds of acetaldehyde with three other aliphatic acid halides

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[1] *Ann.*, 102, 94 (1857).

[2] *Ibid.*, 109, 156 (1859).

[3] *Recueil*, 1, 243 (1882).

[4] *Ber.*, 9, 304 (1876).

were made by Rubencamp[1] and later the corresponding compounds from acetyl chloride and bromide and formaldehyde were prepared by Henry.[2] Recently Staudinger[3] found that addition compounds were formed by oxalyl chloride or bromide with benzaldehyde, and by oxalyl chloride with cinnamic aldehyde. This completes what has been done on these substances in the aliphatic series. Three papers, however, have appeared in which compounds of the above type have probably been involved as intermediate products. Thus Lees[4] in attempting to separate some higher ketones from alcohols by means of benzoyl chloride, found that the ketones reacted with the acid halide. On further investigation he showed that several ketones when boiled with benzoyl chloride or with aliphatic acid chlorides of high molecular weight such as valerianyl chloride evolved hydrochloric acid and yielded presumably the ester of the enolic form of the ketone. Although no intermediate products were isolated, the probability is that addition compounds first formed and then decomposed, giving ethylene derivatives and hydrochloric acid. Descude[5] in studying the action of anhydrous zinc chloride as a catalyst noticed that it increased the speed with which certain aldehydes and ketones reacted, but he did not isolate any definite addition compounds. Paal[6] treated a mixture of acid halides and aldehydes with zinc dust and obtained products which indicated addition had first taken place, but he did not attempt to separate any intermediate products.

In the aromatic series, Claisen[7] found that benzoyl bromide and benzaldehyde reacted to give a crystalline solid, quite unstable, which he suggested was perhaps $C_6H_5CHBrOCOC_6H_5$. This same substance had been obtained much earlier by Liebig[8] when he allowed bromine to react with benzaldehyde, but he supposed the product to be benzoyl bromide. Laurent[9] obtained the analogous chlorine compound as a by-product in the action of chlorine on benzaldehyde and Schiff[10] mentioned that it could be obtained by the action of benzoyl chloride on benzaldehyde. The corresponding iodide, an unstable solid, was probably obtained by Staudinger[11] when he treated benzoyl iodide with benzaldehyde. No other aromatic substances of this type have appeared in the literature.

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[1] *Ann.*, **225**, 274 (1884).

[2] *Bull. acad. roy. belg.*, **1900**, p. 48.

[3] *Ber.*, **42**, 3966 (1909); **46**, 1425 (1913).

[4] *J. Chem. Soc.*, **83**, 14 (1903).

[5] *Ann. chim.*, [7] **29**, 488 (1903).

[6] *Ber.*, **15**, 1818 (1882); **17**, 911 (1884).

[7] *Ibid.*, **14**, 247 (1881).

[8] *Ann.*, **3**, 266 (1832).

[9] *Compt. rend.*, **31**, 113 (1850).

[10] *Ann.*, **154**, 347 (1870).

[11] *Ber.*, **46**, 1425 (1913).

The lack of investigation of these compounds has undoubtedly been due, in part, to the fact that the products from benzoyl chloride and aromatic aldehydes are generally oils, which cannot be made to solidify at all, or only with great difficulty, under the ordinary conditions, and cannot be distilled without decomposition even under diminished pressure. For this research, therefore, which is intended to be preliminary to a more extended study of these compounds, substituted benzoyl chlorides, benzoyl bromide and oxalyl bromide were chosen because they give, in general, solid compounds with aromatic aldehydes.

Preparation of the Addition Compounds.

The substances in this investigation were made merely by bringing together equal molecules of the aldehyde and acid halide (in the case of oxalyl bromide two molecules of aldehyde to one of halide) and allowing the mixture to stand in a well-stoppered flask until solidification took place. This method of preparation for the aromatic addition compounds is quite different from the method used for synthesizing the corresponding aliphatic compounds. To produce the latter, it is necessary to heat the acid halide with the aldehyde, in many cases under pressure, in order to cause the reactions to take place. Oxalyl bromide resembles the aromatic rather than the aliphatic acid halides in this respect and reacts very readily with two molecules of aromatic aldehyde.

The individual compounds differ greatly among themselves in the ease of formation; thus benzoyl bromide and benzaldehyde react to give a solid product in the course of a day or two, while benzoyl bromide and methylvanillin evolve much heat and solidify in a few hours. On the other hand, benzoyl bromide and acetvanillin react more slowly than the benzoyl bromide and methylvanillin and with practically no heat effect. Benzoyl bromide and anisaldehyde combine more rapidly than benzoyl bromide and nitroanisaldehyde; benzoyl bromide and piperonal more rapidly than benzoyl bromide and bromopiperonal. The nitrobenzoyl chlorides and benzaldehyde give solid products after standing together for about a week. From the results obtained it is evident that no general conclusion can be drawn as to the effect of various groups on the speed of formation of the addition compounds, particularly since it seems probable that supercooling takes place in the formation of some of the products, and that if inoculated, solidification would occur more quickly. The indications are, however, that negatively substituted acid halides or aldehydes enter into the addition reactions less easily and less rapidly than the unsubstituted ones.

The products from oxalyl bromide and aromatic aldehydes show the same variance in speed of formation among themselves as the compounds from aromatic acid halides. Since the oxalyl bromide products are higher melting and in general less soluble than the aromatic acid halide products, the reactions proceed more smoothly and quickly. In fact, in several instances, it was found advisable to have a solvent present during the formation.

Constitution of the Addition Compounds.

The product formed from benzoyl bromide and benzaldehyde was chosen as a typical example of this class of compounds and its structure studied. It proved to be phenylbromomethylbenzoate,

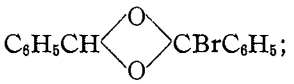
$$C_6H_5CHBrOCOC_6H_6,$$

and, therefore, the conclusion was drawn that all these substances are halogen substituted esters of the general formula

$$RCHXOCOR \quad \text{or} \quad RCHXOCOCOOCHXR$$

if oxalyl halides have been used.

For the benzoyl bromide-benzaldehyde addition compound, there are only three formulas which will explain, first, the comparative instability of the compounds, and, second, the fact that they act in many cases like simple mixtures of benzaldehyde and benzoyl bromide. These formulas are

(1) 

$$C_6H_5CH\langle O_2 \rangle CBrC_6H_5;$$

(2) $C_6H_5C(OH)BrCOR$;

(3) $C_6H_5CHBrOCOC_6H_5$.

The first, mentioned in Beilstein, involves a 4-membered ring containing two ether linkages, a very uncommon and unlikely structure; the second assumes a hydroxyl group and halogen atom on the same carbon atom, a structure which is extremely unstable, so that compounds containing this grouping cannot be isolated. Both these formulas have therefore been discarded. No. 3 is the most reasonable formula and has proven to be the right one. The halogen in the addition compounds reacts with the silver salts of organic acids to give silver bromide, and to substitute the acid residue. By allowing silver benzoate to react with the benzoyl bromide-benzaldehyde compound, benzylidene dibenzoate, a known substance should be produced, provided No. 3 is the correct formula of the addition product. In the laboratory this experiment was carried out and benzylidene dibenzoate was actually formed with quantitative yield.

$$C_6H_5CHBrOCOC_6H_5 + C_6H_5COOAg = AgBr + C_6H_5CH(OCOC_6H_5)_2.$$

The conclusion has therefore been drawn that all these substances are halogen substituted esters.

Reactions of the Addition Compounds.

The investigation of the reactions of these addition compounds has as yet been carried out only in a preliminary way and but one or two individual substances have been carefully studied. The action of water, alcohol, ammonia, primary aromatic amines and silver salts of organic acids has been tested.

With water, all the substances decompose into the aldehyde, organic acid and halogen acid.

$$RCHXOCOR' + H_2O = RCHO + HX + R'COOH.$$

The difference in rate of decomposition, however, is very marked. Some of the compounds, such as those formed from oxalyl bromide and furfural or benzoyl bromide and anisaldehyde decompose in air within a few seconds. On the other hand, the nitro-substituted benzoyl chlorides form addition products which are stable for a long time in cold water or even in dil. sodium carbonate solution. In general, the indications are that those substances which form with difficulty are more stable towards moisture or water.

Cold, absolute alcohol affects the phenylbromomethylbenzoate only very slowly, and in the course of 15 to 20 hours decomposes it, giving as principal products the aldehyde, organic acid ester and halogen acid.

$$C_6H_5CHBrOCOC_6H_5 + C_2H_5OH = C_6H_5CHO + HBr + C_6H_5COOC_2H_5.$$

With ammonia in dry ether as a solvent, the addition compound immediately reacts to give benzamide, benzaldehyde and ammonium bromide.

$$C_6H_5CHBrOCOC_6H_5 + 2NH_3 = C_6H_5CHO + NH_4Br + C_6H_5CONH_2.$$

With aniline in dry ether, however, an entirely different type of reaction takes place. Phenylbromomethylaniline and benzoic acid form in quantitative yield according to the following equation:

$$\begin{array}{l} C_6H_5CHBrOCOC_6H_5 + C_6H_5NH_2 = C_6H_5CHBrNHC_6H_5 + C_6H_5COOH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow NaOH \\ \qquad\qquad\qquad\qquad\qquad C_6H_5CH = NC_6H_5 + NaBr + H_2O \end{array}$$

Not a trace of benzanilide can be detected, showing that no dissociation into benzoyl bromide and benzaldehyde precedes the reaction with aniline. The analogous condensation with *o*-toluidine goes smoothly and a quantitative yield of phenylbromomethyl-*o*-toluidine results. The action of other amines has not yet been studied.

The reaction of phenylbromomethylbenzoate with silver benzoate to give benzylidene dibenzoate has already been mentioned. A few other analogous experiments have been tried, all of which lead to the conclusion that these compounds react readily with the silver salts of organic acids to give silver halide and a compound where the halogen is replaced by the acid residue. Phenylbromomethylbenzoate condenses readily in ether solution with silver benzoate, acetate, chloroacetate and propionate. *p*-Nitrophenylchloromethylbenzoate also condenses readily with silver benzoate.

In conclusion, it may be said that some of the reactions thus far studied show that these addition compounds act almost the same as would mechanical mixtures of benzoyl bromide and benzaldehyde. Other reactions, however, such as with the silver salts of organic acids or with aromatic amines, seem to be characteristic of the addition compounds.

Experimental.

To prepare these addition compounds, equimolecular amounts of the aromatic acid halide and aromatic aldehyde are mixed and allowed to stand at room temperature in a tightly stoppered flask until solidification occurs. In general, the crude products are washed with a little dry ether, or petroleum ether, or with a mixture of the two, and then recrystallized. Ligroin and sometimes chloroform are the solvents most often used. Oxalyl bromide reacts even more readily with the aromatic aldehydes than the aromatic acid halides and yields comparatively high melting and insoluble compounds. In the reactions with oxalyl bromide, it is an advantage in many cases to use a solvent such as dry ether or petroleum ether from which, because of this insolubility, the addition compounds separate in a pure state. Sometimes the formation of these substances takes place at room temperature, at other times at the boiling point of the ether. Owing to the fact that in many cases these addition compounds are rapidly decomposed in air, it is sometimes difficult to get them ready for analysis in perfectly pure form. This has resulted in the acceptance of some of the analyses that are further from the theoretical value than is usually considered entirely satisfactory. The products prepared in this investigation are white except when otherwise described.

REACTIONS OF BENZOYL BROMIDE AND AROMATIC ALDEHYDES.

Benzoyl Bromide and *o*-Bromobenzaldehyde.

o-Bromobenzaldehyde was prepared by heating to 90° *o*-bromotoluene in a flask fitted with a reflux condenser. Two molecules of bromine were slowly dropped in, using sunlight to catalyze the reaction. After the first molecule had been added, the reaction proceeded more slowly and the temperature was gradually raised to 150°. The total process took about 4 hours. The crude reaction mixture was put in a 3-liter flask with 500 cc. water and 150 g. calcium carbonate, refluxed 8 hours, and then steam distilled. The distillate was extracted with ether, the ether was evaporated and the residual mass was treated with excess of sodium bisulfite solution. Undissolved material was filtered off and the solution made alkaline with sodium carbonate solution and steam-distilled. A pure substance in 80% yields, and boiling at 230°, was obtained.

When this was mixed with benzoyl bromide, solidification took place in 7 hours. A quantitative yield of material resulted which gave crystals from ligroin; m. p., 106–107°. Only slight decomposition occurred on standing in air for several days.

Subst., 0.2364; AgBr, 0.2441.
Calc. for $C_{14}H_{10}O_2Br_2$: Br, 43.24. Found: 43.90.

Benzoyl Bromide and *p*-Bromobenzaldehyde.

p-Bromobenzaldehyde was prepared from *p*-bromotoluene by exactly the same method employed for preparing *o*-bromobenzaldehyde from *o*-bromotoluene which has just been described above. M. p., 56–57°; yield, 80%.

With benzoyl bromide solidification took place in 3 hours. A quantitative yield resulted which gave crystals from ligroin; m. p., 110°. These decomposed slightly after standing in air ten hours.

Subst., 0.1978; AgBr, 0.2023.
Calc. for $C_{14}H_{10}O_2Br_2$: Br, 43.24. Found: 43.54.

Benzoyl Bromide and Nitroanisaldehyde.

Nitroanisaldehyde was prepared by the nitration of anisaldehyde below 0° according to the method of Einhorn and Grabfield[1] and of Worner.[2] After several crystallizations from dil. alcohol, the nitroanisaldehyde melted at 72–73°. The melting points given by the above investigators are 83.5° and 72°, respectively. The yield was 8 g. from 15 g. of anisaldehyde.

Mixed with benzoyl bromide, solid formed in 3 hours in quantitative yield, giving crystals from ligroin; m. p., 101–102°. The substance decomposed only very slowly in the air.

Subst., 0.1630; AgBr, 0.0817.
Calc. for $C_{15}H_{12}O_5NBr$: Br, 21.86. Found: 21.33.

Benzoyl Bromide and Acetvanillin.

The acetvanillin was made by shaking the sodium salt of vanillin with an ether solution of acetic anhydride according to the method of Tiemann and Nagai.[3] Ten g. vanillin yielded 8 g. acetvanillin; m. p., 75–76°.

Benzoyl bromide and acetvanillin solidified within a few hours. The yield of product was 75% and gave crystals from ligroin; m. p., 102–103°, which decomposed slowly in the air.

Subst., 0.2111; AgBr, 0.1056.
Calc. for $C_{17}H_{15}O_4Br$: Br, 21.12. Found: 21.27.

Benzoyl Bromide and *p*-Nitrobenzaldehyde.

When these two compounds reacted, crystals formed in one day. After recrystallization from ligroin, the material melted at 89–90°, but neither ligroin nor any of the common solvents was perfectly satisfactory as

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[1] *Ann.*, **243**, 370 (1888).

[2] *Ber.*, **29**, 157 (1896).

[3] *Ibid.*, **11**, 647 (1878).

solvent. The crystals were quite stable in the air. On account of the small quantity available no analysis was made.

Benzoyl Bromide and Bromopiperonal.

The bromopiperonal was prepared by the method of Oelker.[1] When mixed with benzoyl bromide, a red magma formed after standing several hours; white crystals were obtained from ligroin; m. p., 108–113°. The m. p. did not change with further recrystallization, as some decomposition always took place. The crystals decomposed in the air.

Subst., 0.1956; AgBr, 0.1913.

Calc. for $C_{15}H_{10}O_4Br_2$: Br, 38.64. Found: 37.27.

With vanillin or salicylaldehyde, a vigorous reaction took place when benzoyl bromide was added, but apparently the hydroxyl group had been attacked in both instances so that only impure mixtures resulted.

With anisaldehyde and benzoyl bromide a reaction took place but no solid formed. Evidently the product is an oil.

With furfural and benzoyl bromide an extremely vigorous action took place accompanied by considerable charring, and no definite product could be isolated.

Benzoyl Bromide and Terephthalaldehyde.

The mixture crystallized in a few hours; no heat effect was apparent. The resulting material was insoluble in most organic solvents; ethylene chloride was used for the recrystallization, although it was quite unsatisfactory. Crystals formed, m. p. 153–162°, which decomposed slightly on standing in the air. Analysis showed that an impure compound, consisting of two molecules of halide and one of terephthalaldehyde, had been obtained.

Calc. for $C_{22}H_{16}O_4Br_2$: Br, 31.75. Found: Br, 34.60.

Benzoyl Bromide and Piperonal.

The mixture reacted slowly, and after several days some crystals, m. p. 105–110°, had formed. These could be crystallized from ligroin, but at once decomposed in the air to a blue mush, rendering purification impossible.

Benzoyl Bromide and Methyl-Salicylaldehyde.

The methyl ether of salicylaldehyde was prepared by the action of dimethyl sulfate on the sodium salt of salicylaldehyde according to the method of Katschalowsky and Kostanecki,[2] and purified by distillation. 24 g. salicylaldehyde yielded 10 g. of the methyl ether boiling at 225–227°.

The reaction of the aldehyde with benzoyl bromide evolved considerable heat, and the substance crystallized in an hour or two. After washing with a little dry ether and petroleum ether, crystals were obtained

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[1] *Ber.*, 24, 2593 (1891).

[2] *Ibid.*, 37, 2347 (1904).

which melted at about 50°, but decomposed in the air in less than 10 seconds.

Benzoyl Bromide and Methylvanillin.

The methylvanillin was prepared by the action of dimethyl sulfate on the sodium salt of vanillin by the method of Rosenmund.[1]

The reaction of the aldehyde with benzoyl bromide evolved considerable heat. Very unstable crystals were obtained from petroleum ether; m. p., 100°. They decomposed in a few seconds in the air.

REACTION OF AROMATIC ACID CHLORIDES AND AROMATIC ALDEHYDES.

Benzoyl Chloride and Bromomethylvanillin.

Bromovanillin was made by passing a stream of air containing bromine through an alcohol solution of vanillin, according to the method of Tiemann and Haarmann;[2] the yield was quantitative. To prepare the methyl ether, 21 g. bromovanillin was treated with 150 cc. of a 2.5% solution of sodium hydroxide and warmed until nearly all the solid had dissolved. Then 14 g. dimethyl sulfate were added in portions with vigorous shaking. More sodium hydroxide solution was introduced until the reaction mixture became colorless; then 11 g. more dimethyl sulfate was added and finally the whole was heated another half hour. After cooling quickly in ice, the solid was filtered off and boiled with 300 cc. water to remove sodium salts. The methyl ether was filtered off and recrystallized from dilute alcohol; it gave crystals, m. p. 56–58°. Then a milky liquid was formed which cleared up rather sharply at 105°.

The bromomethylvanillin soon went into solution in benzoyl bromide and after standing a week the material had changed to a thick mush. This was washed with a little dry ether, then recrystallized from ligroin to yield crystals, m. p. 158–160°, which were fairly stable in air.

Subst., 0.0732; AgCl + AgBr, 0.0640.
Calc. for $C_{16}H_{14}O_4ClBr$: AgCl + AgBr, 0.0628 g.

Benzoyl Chloride and Bromopiperonal.

The bromopiperonal was prepared by the method of Oelker.[3] On standing for a week, most of the material had solidified. After a number of recrystallizations from ligroin, the melting point remained constant at 97–102°. The crystals slowly decomposed in the air.

Subst., 0.0784; AgCl + AgBr, 0.0711.
Calc. for $C_{15}H_{10}O_4ClBr$: AgCl + AgBr, 0.0702 g.

o-Nitrobenzoyl Chloride and Benzaldehyde.

The materials crystallized a week after mixing. The product was boiled with petroleum ether to remove the sticky substance and the color. Crystals from ligroin were obtained in a yield of 80%; m. p., 81–82°.

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[1] *Ber.*, **43**, 3415 (1910).

[2] *Ibid.*, **7**, 615 (1874).

[3] *Ibid.*, **24**, 2593 (1891).

Subst., 0.1930; AgCl, 0.0925.
Calc. for $C_{14}H_{10}O_4NCl$: Cl, 12.18. Found: 11.88.

m-Nitrobenzoyl Chloride and Benzaldehyde.

The addition compound crystallized out 3 months after mixing the aldehyde and the acid halide, although in a second experiment inoculation of the liquid with a crystal of the substance caused the addition product to crystallize out in 5 or 6 days. A quantitative yield resulted which gave yellow crystals from ligroin, m. p. 87–88°, which were stable in the air.

Subst., 0.2054; AgCl, 0.1024.
Calc. for $C_{14}H_{10}O_4NCl$: Cl, 12.18. Found: 12.35.

p-Nitrobenzoyl Chloride and Benzaldehyde.

The mixture crystallized in 5 days. A quantitative yield of yellow crystals was obtained, which were purified from ligroin, m. p. 118–118.5°, and were stable in air and in water, and even for a short time in cold sodium carbonate solution.

Subst., 0.1858; AgCl, 0.0946.
Calc. for $C_{14}H_{10}O_4NCl$: Cl, 12.18. Found: 12.59.

Halogen Substituted Acid Chlorides and Benzaldehyde.

Mixtures of benzaldehyde with *p*-chlorobenzoyl chloride, *p*-bromobenzoyl bromide, or *o*-bromobenzoyl chloride did not solidify even after standing at 30° for several months. Whether no reaction took place in these 3 cases, or whether the products actually formed but were oils, was not determined.

REACTIONS OF OXALYL BROMIDE AND AROMATIC ALDEHYDES.

Oxalyl bromide was prepared from oxalyl chloride according to the method of Staudinger[1] with an 85% yield. In every case two molecules of aldehyde react with one of oxalyl bromide so that the constituents were always mixed in these proportions.

Oxalyl Bromide and Benzaldehyde.

The addition product was obtained in practically quantitative yield when prepared either in the presence or the absence of a solvent, but was more easily purified if the reaction was carried on in a solvent, for instance, petroleum ether. This has already been described by Staudinger and Anthes.[1] From carbon disulfide crystals were obtained, m. p. 130–131°, which soon decomposed in the air, giving benzaldehyde, hydrobromic acid, carbon dioxide, and carbon monoxide.

Oxalyl Bromide and *o*-Bromobenzaldehyde.

The preparation of *o*-bromobenzaldehyde has been described above.

The mixture of the aldehyde and oxalyl bromide, without any solvent,

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[1] *Ber.*, 46, 1425 (1913).

solidified in 10 hours. A quantitative yield resulted which gave crystals from ligroin; m. p., 140°.

Subst., 0.2107; AgBr, 0.2696.
Calc. for $C_{16}H_{10}O_4Br_4$: Br, 54.60. Found: 54.45.

Oxalyl Bromide and Cinnamic Aldehyde.

The mixture boiled from the heat of reaction when the substances were merely put together and in two hours a gray solid formed. This was washed with dry ether, which left perfectly white crystals. Since these crystals were soluble in ether, however, some material was lost, and the yield was only 50% of theory; m. p., 85–86°. When recrystallized from benzene instead of washing with ether, the yield was better, but the crystals obtained decomposed much more rapidly. In either case, the material quickly decomposed in air.

Subst., 0.2576; AgBr, 0.2056. Subst., 0.1976; CO_2, 0.3649; H_2O, 0.0616.
Calc. for $C_{20}H_{16}O_4Br_2$: Br, 33.33; C, 50.00; H, 3.33. Found: Br, 33.57; C, 50.36; H, 3.46.

Oxalyl Bromide and Anisaldehyde.

The reaction was carried on in absolute ether solution, using a small excess of oxalyl bromide. Crystals soon began to separate; these were filtered off after two days and washed with a little ether. The yield was almost quantitative; m. p. about 66°, with decomposition. The material was very unstable and decomposed quickly in the air, turning dark and giving off gas. It could not be recrystallized, as it decomposed when slightly heated.

Subst., 0.2800; AgBr, 0.2163.
Calc. for $C_{18}H_{16}O_6Br_2$: Br, 34.18. Found: 32.87.

Oxalyl Bromide and Nitroanisaldehyde.

The reaction without a solvent proceeded with the evolution of some heat. The substance crystallized after 4 days. It was then washed with dry ether and recrystallized from a mixture of one volume of benzene and 4 volumes of ligroin. Crystals resulted, m. p. 116–118°, which showed no appreciable decomposition after standing a day.

Subst., 0.2206; AgBr, 0.1452.
Calc. for $C_{18}H_{14}O_{10}N_2Br_2$: Br, 27.68. Found: 28.02.

Oxalyl Bromide and *m*-Nitrobenzaldehyde.

The reaction was carried out in ether solution and required several hours before solidification took place. The product was purified by dissolving it in hot chloroform and adding 6 times its volume of petroleum ether and cooling. Yellow crystals resulted, m. p. 128–129°, which decomposed slowly in the air.

Subst., 0.2240; AgBr, 0.1675.
Calc. for $C_{16}H_{10}O_8N_2Br_2$: Br, 30.88. Found: 31.80.

Oxalyl Bromide and *p*-Nitrobenzaldehyde.

The two substances showed no reaction after long standing or even after being heated at 50° for a few minutes; unchanged *p*-nitrobenzaldehyde was recovered.

Oxalyl Bromide and Piperonal.

The reaction was carried out in dry ether solution, which boiled while the reaction was going on. In 5 minutes the material solidified. It was washed with a little ether and recrystallized from hot chloroform giving crystals, m. p. 81–83°, unstable in air.

Subst., 0.2092; AgBr, 0.1534.
Calc. for $C_{16}H_{12}O_8Br_2$: Br, 31.01. Found: 31.20.

Oxalyl Bromide and Vanillin.

The reaction was carried on in dry ether and was complete in 5 or 10 minutes. The white crystals were filtered and recrystallized from ligroin. A 90% yield of material, m. p. 93–95° was obtained.

Subst., 0.2110; AgBr, 0.1551.
Calc. for $C_{18}H_{16}O_8Br_2$: Br, 30.77. Found: 31.30.

Oxalyl Bromide and Acetvanillin.

The mixture solidified after standing two hours. The crystals were purified by dissolving in chloroform and precipitating with petroleum ether. The substance had a m. p. of 142–143° with decomposition and underwent only slight decomposition on standing in the air for a day.

Subst., 0.1049; AgBr, 0.0650.
Calc. for $C_{22}H_{20}O_{10}Br_2$: Br, 26.49. Found: 26.37.

Oxalyl Bromide and Furfural.

The reaction was carried on by adding the furfural to about 6 times its weight of petroleum ether, then introducing just enough dry ether to take the furfural into solution. Oxalyl bromide was added, and soon crystals deposited on the walls of the flask; in about an hour the reaction was complete. The crystals were unstable and quickly turned dark on standing or when heated to 40°. Several recrystallizations from ligroin gave white crystals, m. p. 76–77°.

Subst., 0.2287; AgBr, 0.2117.
Calc. for $C_{12}H_8O_6Br_2$: Br, 39.41. Found: 39.42.

REACTIONS OF THE ADDITION COMPOUNDS.

1. With Silver Salts of Organic Acids.

Benzylidene Dibenzoate from Phenylbromomethylbenzoate.—20 g. of the addition compound of benzoyl bromide and benzaldehyde[1] was dissolved in 300 cc. dry ether and an excess of silver benzoate added. The reaction began immediately, causing the ether to boil and silver bromide to separate. The ether solution was filtered off and evaporated,

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[1] *Ber.*, 14, 2475 (1881).

leaving 16 g. of a yellow liquid which could not be crystallized and which decomposed into benzaldehyde and benzoic anhydride when distilled under 31 mm. pressure. Accordingly, some benzylidene dibenzoate was prepared from benzaldehyde and benzoic anhydride according to the method of Wegscheider and Spath.[1] After 3 crystallizations from petroleum ether, the crystals melted at 62–63° (Wegscheider gives 61–62°). When one of these crystals was used to inoculate the liquid obtained by the action of silver benzoate on the addition product, the mixture quickly crystallized. The product was benzylidene dibenzoate, as shown by its properties, and by a mixed melting point with the same substance prepared from benzaldehyde and benzoic anhydride. The analysis of the product for carbon and hydrogen at first came high, indicating that petroleum ether had not been completely removed. After heating the material to 100° for 8 hours or more, however, the analyses were good.

Subst., 0.1736; CO_2, 0.4832; H_2O, 0.0788.
Calc. for $C_{21}H_{16}O_4$: C, 75.90; H, 4.82. Found: C, 75.91; H, 5.04.

The addition compound of benzaldehyde and benzoyl bromide was therefore phenylbromomethylbenzoate.

Benzylidene Acetate Benzoate from Phenylbromomethylbenzoate.—The reaction between silver acetate and phenylbromomethylbenzoate was carried out in the same way as the reaction between silver benzoate and phenylbromomethylbenzoate. 13 g. phenylbromomethylbenzoate gave 16 g. of a viscous liquid which gradually crystallized to a white solid. After several recrystallizations from ligroin, the substance melted at 71–72°.

Subst., 0.2138; CO_2, 0.5556; H_2O, 0.1039.
Calc. for $C_{16}H_{14}O_4$: C, 71.11; H, 5.19. Found: C, 70.86; H, 5.40.

An attempt was made to synthesize the same compound by the method of Wegscheider and Spath; benzoic acetic anhydride was heated with benzaldehyde in the presence of a small amount of sulfuric acid, but the only product obtained was benzylidene dibenzoate.

With silver propionate and silver chloroacetate, phenylbromomethylbenzoate reacted readily, but the products could not be made to crystallize, and they decomposed when distilled.

Benzylidene Benzoate *p*-Nitrobenzoate from *p*-Nitrophenylchloromethylbenzoate.—The addition product of benzaldehyde and *p*-nitrobenzoyl chloride was treated with silver benzoate in dry ether. The product obtained was recrystallized from a mixture of a little dry ethyl ether and petroleum ether to give yellow crystals, m. p. 65–67°.

Subst., 0.1672; N_2, 7.7 cc. at 20° and 723.5 mm.
Calc. for $C_{16}H_{13}O_6N$: N, 4.44. Found: 4.76.

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[1] *Monatsh.*, **30**, 862 (1909).

The method of Wegscheider and Spath was also tried in an attempt to synthesize the above compound. The benzoic *p*-nitrobenzoic anhydride was made by heating equivalent quantities of the sodium salt on *p*-nitrobenzoic acid and benzoyl chloride for several hours on the water bath. It was purified by dissolving it in hot chloroform and adding petroleum ether until a turbidity appeared, then cooling. The yellow anhydride, m. p. 127–133°, readily crystallized out. When this was treated with benzaldehyde and a small amount of sulfuric acid and heated, however, the mixture decomposed and no pure product could be isolated.

2. With Ammonia and Amines.

Phenylbromomethylbenzoate and Ammonia.—Dry ammonia gas was led into a dry ether solution of phenylbromomethylbenzoate until no more white solid separated. The solid was filtered off and the ether evaporated from the filtrate, giving 6 g. of benzaldehyde. The solid, weighing 13 g. was a mixture of ammonium bromide and benzamide. On extraction with hot benzine, the benzamide was dissolved and crystallized out on cooling.

Phenylbromomethylbenzoate and Aniline.—When equivalent quantities of phenylbromomethylbenzoate and aniline were mixed, a great deal of heat was evolved by the reaction. A yellow solid was formed which was stable in air and soluble in water. The solid was extracted with ether and pure benzoic acid was obtained from the extract. The other insoluble solid was analyzed for bromine. It proved to be phenylbromo ethylaniline.

Subst., 0.2052; AgBr, 0.1504.
Calc. for $C_{13}H_{12}NBr$: Br, 30.53. Found: 31.19.

Some of the solid material was then treated with sodium hydroxide solution, and an oil separated. This was taken up in ether, the ether evaporated, and a solid substance, benzylidene aniline, m. p. 45–48°, b. p. 300–305°, was obtained.

Subst., 0.2051; N_2, 14.6 cc. at 20° and 731 mm.
Calc. for $C_{13}H_{11}N$: N, 7.74. Found: 7.97.

The other physical and chemical properties of the compound agreed with those of benzylidene aniline.

Phenylbromomethylbenzoate and *o*-Toluidine.—Phenylbromomethylbenzoate reacted in the same way with *o*-toluidine, giving benzylidene *o*-toluidine, which is an oil at 0°, b. p. 210–212° under 72 mm.

Subst., 0.2526; N_2, 16.2 cc. at 21° and 734.5 mm.
Calc. for $C_{14}H_{13}N$: N, 7.2. Found: 7.2.

Dimethyl aniline and phenylbromomethylbenzoate evolved much heat and a green resinous product resulted.

3. With Water and Alcohol.

Phenylbromomethylbenzoate gradually dissolved in ethyl alcohol After standing a day, the solution was distilled *in vacuo* and benzaldehyde and ethyl benzoate were obtained as the main products, although some unidentified halogen compounds were present in small amounts.

The instability of many of these addition compounds in air has already been mentioned. This is undoubtedly due to the presence of moisture present in the air. The stability in water varies in same way as the stability in air. All will subsequently decompose to give benzoic acid, halogen acid, and benzaldehyde.

Summary.

1. The reaction between aromatic aldehydes and aromatic acid halides seems to be a general one.

(*a*) Benzoyl bromide, (*b*) benzoyl chloride and a number of its substitution products, (*c*) oxalyl bromide have been condensed with various aromatic aldehydes.

2. The substances formed are addition compounds of one molecule of acid halide and one molecule of aldehyde (in the case of oxalyl bromide, one molecule of acid halide to two of aldehyde).

3. The constitution of the substances is represented by the general formula RCHXOCOR (or RCHXOCOCOOCHXR if oxalyl halides are used).

4. These compounds have been treated with water, alcohol, ammonia, certain amines and silver salts of organic acids. In some cases the reactions are those to be expected from a mere mixture of acid halide and aldehyde, in other cases are characteristic of these substances.

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ZIRCONYL BASIC BENZOATES AND SALICYLATES.

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Nothing definite has appeared in the literature as to the composition of compounds of zirconium and benzoic or salicylic acids. The formation of certain precipitates only has been mentioned by Mandl.[1] Rosenheim and Hertzman[2] have, by the action of benzoic acid upon zirconium tetrachloride in ether solution, prepared a compound $ZrCl_2(C_6H_5.CO_2)_2$. We have subjected these basic salts to examination, so far as time allowed, with the following results: It may be stated that the chief interest attaches to the general behavior of zirconium, or rather the radical zirconyl, toward organic acids, which has been only imperfectly studied. Apologies should be offered for the incompleteness of this present study. It has

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[1] *Z. anorg. Chem.*, **37**, 252 (1903).

[2] *Ber.*, **40**, 812 (1907).