to a benzene solution of copper oleate caused a momentary increase in the galvanometer reading followed by a decrease to somewhat less than the original reading.

A solution of oleic acid, in dry benzene, after drying over anhydrous copper sulfate, showed practically no conductivity. The addition of hydrogen chloride to this solution increased the reading only slightly. Upon treating it with a benzene solution of stannic chloride, however, the conductivity was increased to such an extent that no reading could be taken with the instruments used.

The conductivity shown in these cases is considered sufficient to account for the reactivity of the solutions on the basis of the dissociation theory.

LAWRENCE, KANSAS.

THE REACTION BETWEEN ACID HALIDES AND ALDEHYDES. II.

BY H. E. FRENCH WITH ROGER ADAMS.[1]
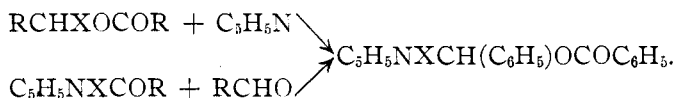
In an earlier paper from this laboratory,[2] the fact was brought out that many aromatic aldehydes and aromatic acid halides react readily to form halogenated benzyl benzoates and a study of a number of the reactions of these condensation products was made. In the present communication this work has been extended.

It has been shown that the reaction between aromatic acid halides and the aromatic aldehydes is very general. The previous work indicated that in a few instances perhaps, certain aromatic aldehydes would not condense with certain aromatic acid halides to give the expected derivatives. This conclusion resulted from the fact that solid products could not be isolated although from the nature of the substituents solid products might be expected. The oils which were produced always decomposed when vacuum distillation was attempted so that it was impossible to determine whether a definite substance existed or whether merely a mechanical mixture. By treating these oily reaction mixtures with pyridine, solid addition compounds of pyridine and the aldehyde-acid halide products were formed and easily purified. Thus it was shown that a reaction actually had taken place in these instances and the resulting products were oils. Moreover the aldehyde-acid halide condensation products which were solids but too unstable to purify and analyze could be isolated in the form of stable pyridine addition products. These same pyridine addition products could be made also by first treating pyridine with an acid-halide and then adding the aldehyde.

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[1] This communication is an abstract of work carried out by H. E. French in partial fulfilment for the degree of Doctor of Philosophy at the University of Illinois.

[2] THIS JOURNAL, **40**, 1732 (1918).

$$\begin{array}{c} RCHXOCOR + C_5H_5N \\ \\ C_5H_5NXCOR + RCHO \end{array} \Big\rangle C_5H_5NXCH(C_6H_5)OCOC_6H_5.$$

Trimethylamine formed addition products in a similar manner to pyridine, and presumably any other aliphatic tertiary amine would react similarly.
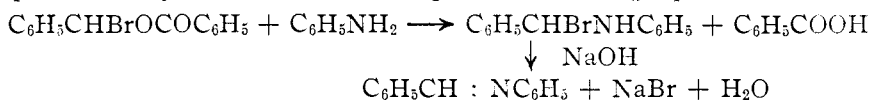
The large number of aromatic aldehydes and aromatic acid halide compounds produced, allowed definite conclusions to be drawn in regard to the ease of formation. In general the acid halides or aldehydes containing a chlorine, bromine, iodine or nitro group reacted more slowly to give addition products than those acid halides and aldehydes which were unsubstituted or contained methyl or methoxy groups. On the other hand the former class yielded much more stable products than were formed in the latter class. If a methoxy or methyl group was present the resulting halogenated esters, even though the phenyl groups contained a halogen or nitro group in addition, were quite unstable substances. Aromatic aldehydes did not react as rapidly with aromatic acid chlorides as with the corresponding acid bromides. It appeared, moreover, that with the acid chlorides the addition reactions did not run so nearly to completion as with the acid bromides; in many cases, the acid chlorides and aldehydes gave only semi-solid reaction masses even after several days' standing.

It seems apparent that the reaction between the acid halides and aldehydes to form the halogenated esters is an equilibrium reaction, the equilibrium point depending on the nature of the initial substances and of the product. Sometimes the reactions ran almost to completion, in other cases only part way. The latter type was particularly noticeable with the acid chlorides. Many of the pure halogenated esters, although kept in a dry place changed within a few days to a semi-solid mass which appeared similar to that formed by the addition of the acid halide to the aldehyde. A trace of zinc chloride greatly speeded up the reactions and caused the equilibrium point to be reached in a comparatively short time. The tendency of these halogenated esters to dissociate accounts for a number of their reactions, especially those which might be expected providing these compounds were merely mixtures of acid halide and aldehyde.

A preliminary study of the reactions of these addition compounds was made by Adams and Vollweiler.[1] It was found that with water, the addition compounds behaved as a simple mixture of acid halide and aldehyde producing hydrobromic acid, organic acid and aldehyde; with alcohol, a similar reaction took place, with the formation of an ester, aldehyde and hydrobromic acid; with ammonia in dry ether solution there resulted an acid amide, aldehyde and ammonium bromide; with

[1] Adams and Vollweiler, THIS JOURNAL, 40, 1732 (1918).

aniline, the organic acid and phenyl-bromomethyl aniline in practically quantitative yields formed according to the following equation:

$$C_6H_5CHBrOCOC_6H_5 + C_6H_5NH_2 \longrightarrow C_6H_5CHBrNHC_6H_5 + C_6H_5COOH$$
$$\downarrow \ NaOH$$
$$C_6H_5CH : NC_6H_5 + NaBr + H_2O$$

In the present research, the action of different amines has been investigated; o- and p-chloro-anilines, o- and p-toluidines all give analogous results to aniline itself. As a type of primary aliphatic amine, methyl amine was chosen. In dry ether solution, bromomethyl benzoate with this amine yields methyl benzamide, methyl amine hydrobromide and benzylidene methyl amine.

$$C_6H_5CHBrOCOC_6H_5 + 3CH_3NH_2 \longrightarrow$$
$$C_6H_5CONHCH_3 + CH_3NH_2 \cdot HBr + C_6H_5CH = NCH_3 + H_2O.$$
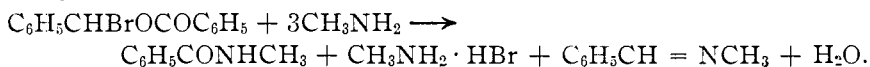
Secondary aliphatic amines, such as diethyl amine, give a mixture of disubstituted acid amide, aldehyde and salt of the amine.

$$C_6H_5CHBrOCOC_6H_5 + 2(C_2H_5)_2NH \longrightarrow$$
$$C_6H_5CON(C_2H_5)_2 + C_6H_5CHO + (C_2H_5)_2NH.HBr.$$
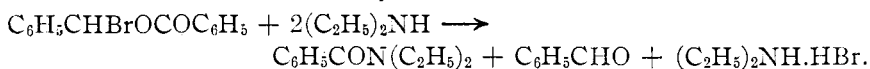
Tertiary aliphatic amines, such as trimethyl amine, give addition compounds; pyridine acts in a similar manner as has already been mentioned. With secondary and tertiary aromatic amines, complex substances belonging to the triphenyl methane series are produced.

These halogenated esters in dry ether react with zinc or copper powder to give condensation products which are derivatives of the dibenzoate of hydrobenzoin.[1]

$$2C_6H_5CHBrOCOC_6H_5 + Zn \longrightarrow (C_6H_5CHOCOC_6H_5)_2 + ZnBr_2.$$
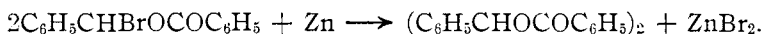
Many side reactions, however, take place, so that the yields seldom are greater than 20%.

The addition compounds react with potassium cyanide, alkali salts of organic acids or potassium hydroxide to give more or less complete hydrolysis. Definite compounds from these reactions have not been isolated.

Experimental.

To prepare the addition compounds, equimolecular amounts of the acid halide and aldehyde were mixed and allowed to stand at room temperature in a tightly stoppered flask. More or less heat was invariably evolved and in the course of from a few minutes up to several days, the mixtures became solid or semi-solid and did not change on further standing. The products were washed with a little dry ether or petroleum ether, powdered and then recrystallized. It was noticeable that the acid bromides in most cases formed solids with the aldehydes while in general, the acid chlorides formed semi-solids with the aldehydes. The times for the reactions given in the following tables represent the maximum time necessary after which no further change in the mixture was noticed. When a small amount of anhydrous zinc chloride was added, the time required for reaching the end of the reaction was greatly diminished.

The compounds and their constants and analyses are given in the following table.

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

Name of compounds and reacting materials.	Time for reaction. Hours.	Solvent cryst.	M. p. ° C.	Analyses.			
						Halogen.	
				Subs. G.	Ag halide. G.	Calc. %.	Found. %.
1. Phenyl-bromomethyl-*m*-nitrobenzoate from *m*-nitrobenzoyl bromide and benzaldehyde.....................................	15	ligroin	94–6	0.1062	0.0596	23.81	23.87
2. Phenyl-bromomethyl-*p*-nitrobenzoate from *p*-nitrobenzoyl bromide and benzaldehyde.....................................	30 min.	ligroin	139–40	0.1987	0.1123	23.81	24.05
3. *o*-Bromophenyl-bromomethyl-*p*-nitrobenzoate from *p*-nitrobenzoyl bromide and *o*-bromobenzaldehyde......................	15	petr. ether	140–2	0.2026	0.1809	38.55	37.99
4. *p*-Bromophenyl-bromomethyl-*p*-nitrobenzoate from *p*-nitrobenzoyl bromide and *p*-bromobenzaldehyde......................	5 min.	ligroin	146	0.2026	0.1812	38.55	38.05
5. Phenyl-bromomethyl-3,5-dinitrobenzoate from 3,5-dinitrobenzoyl bromide and benzaldehyde..............................	1	ligroin	126–7	0.2096	0.1056	20.99	21.43
6. *p*-Bromophenyl-bromomethyl-3,5-dinitrobenzoate from 3,5-dinitrobenzoyl bromide and *p*-bromobenzaldehyde...............	2	ligroin	151–2	0.1953	0.1590	34.78	34.64
7. *o*-Bromophenyl-bromomethyl-3,5-dinitrobenzoate from 3,5-dinitrobenzoyl bromide and *o*-bromobenzaldehyde...............	100	ligroin	119–22	0.2047	0.1690	34.78	35.13
8. Phenyl-bromomethyl-*o*-chlorobenzoate from *o*-chlorobenzoyl bromide and benzaldehyde...............................	70	petr. ether	62–3	0.2006	0.2042	...	0.2042
9. Phenyl bromomethyl-*p*-chlorobenzoate from *p*-chlorobenzoyl bromide and benzaldehyde...............................	3	ligroin	110–1	0.1590	0.1654	...	0.1619
10. Phenyl-bromomethyl-*o*-bromobenzoate from *o*-bromobenzoyl bromide and benzaldehyde...............................	15	ligroin	80	0.1955	0.1974	43.24	42.96
11. *p*-Bromophenyl-bromomethyl-*o*-bromobenzoate from *o*-bromobenzoyl bromide and *p*-bromobenzaldehyde...................	40 min.	ligroin	102–3	0.1981	0.2506	53.45	53.82
12. Phenyl-bromomethyl-*p*-bromobenzoate from *p*-bromobenzoyl bromide and benzaldehyde........	15	ligroin	119–21	0.2013	0.2028	43.24	42.87
13. *o*-Bromophenyl-bromomethyl-*p*-bromobenzoate from *p*-bromobenzoyl bromide and *o*-bromobenzaldehyde...	5	ligroin	154–6	0.1965	0.2470	53.45	53.48

14. *p*-Bromophenyl-bromomethyl-*p*-bromobenzoate from *p*-bromobenzoyl bromide and *p*-bromobenzaldehyde	1	ligroin	120–1	0.2000	0.2511	53.45	53.42
15. Phenyl-bromomethyl-*p*-iodobenzoate from *p*-iodobenzoyl bromide and benzaldehyde	4	ligroin	123–4	0.2032	0.2068	...	0.2060
16. *β*-Phenyl-vinyl bromo-methyl *m*-nitrobenzoate from *m*-nitrobenzoyl bromide and cinnamyl aldehyde							
17. *p*-Methoxyphenyl bromo-methyl *p*-nitrobenzoate from *p*-nitrobenzoyl bromide and anisaldehyde							
18. Phenyl-bromomethyl-*m*-chlorobenzoate from *m*-chlorobenzoyl bromide and benzaldehyde							
19. *p*-Methoxyphenyl-bromomethyl-*p*-bromobenzoate from *p*-bromobenzoyl bromide and anisaldehyde		These substances were all solids but decomposed so easily that under ordinary conditions they could not be purified for analysis.						
20. Phenyl-bromomethyl-*p*-methoxybenzoate from anisyl bromide and benzaldehyde							
21. Phenyl-bromomethyl-*o*-methylbenzoate from *o*-methylbenzoyl bromide and benzaldehyde							
22. Phenyl-bromomethyl-*m*-methylbenzoate from *m*-methylbenzoyl bromide and benzaldehyde							
23. *p*-Bromophenyl-chloromethyl benzoate from benzoyl chloride and *p*-bromobenzaldehyde	100	ligroin	109–10	0.2020	0.2071	...	0.2057
24. Phenyl-chloromethyl 3,5-dinitrobenzoate from 3,5-dinitribenzoyl chloride and benzaldehyde	50	ethyl acetate	135–6	0.1993	0.0872	10.55	10.82
25. *p*-Bromophenyl-chloromethyl 3,5-dinitrobenzoate from 3,5-dinitrobenzoyl chloride and *p*-bromobenzaldehyde	200	ligroin	145–6	0.2000	0.1570	...	0.1595
26. *p*-Bromophenyl-chloromethyl-*p*-bromobenzoate from *p*-bromobenzoyl chloride and *p*-bromobenzaldehyde	24	ligroin	124–5	0.2032	0.2578	...	0.2609
27. Phenyl-chloromethyl cinnamate from cinnamyl chloride and benzaldehyde	72	ligroin	80	0.1968	0.1048	13.02	13.16
28. *p*-Bromophenyl-chloromethyl cinnamate from cinnamyl chloride and *p*-bromobenzaldehyde	3	ligroin	92–3	0.2043	0.1926	...	0.1925

Phenyl Chloromethyl Benzoate, $C_6H_5COOCHClC_6H_5$.[1]

Upon mixing benzoyl chloride and benzaldehyde together with a small piece of fused zinc chloride, a reaction took place at once and heat was developed. No solid formed, however, even after long standing and thorough chilling. The resulting oil was fractionated as follows:

1st fraction, boiling 77–81° at 15 mm.
2nd fraction, boiling 84–86° at 15 mm.
3rd fraction, boiling 205–208° at 15 mm.

The first and second fractions proved to be benzaldehyde and benzoyl chloride, respectively. The third fraction which solidified proved to be benzoic anhydride.

In addition to the above chlorinated esters, (Nos. 22–28 in the table) those produced from cinnamyl chloride and anisaldehyde as well as from cinnamyl chloride and piperonal and methyl vanillin were made. Both were solids but unstable so that they were not purified for analysis.

Compounds Formed from Pyridine and the Acid Halide-Aldehyde Condensation Products.

Phenyl-bromomethyl Benzoate and Pyridine, $C_5H_5NBrCH(C_6H_5)OCOC_6H_5$. —phenyl-bromomethyl benzoate was treated with excess of pyridine. It went into solution slowly, but there was no evidence of a reaction. On standing, however, crystals began to deposit and soon a heavy precipitate had formed. The solid material was filtered off and purified by dissolving in absolute alcohol and precipitating with dry ether. It melted at 180° with decomposition, was very soluble in water and gave a neutral solution. This solution gave an immediate precipitate of silver bromide on the addition of silver nitrate.

Analyses. Subs., 0.5954, 0.5934: 17.14, 17.14 cc. 0.0934 N AgNO₃. Calc. for $C_{19}H_{16}O_2NBr$: Br, 21.62. Found: 21.50, 21.58.

The same compound was also made by adding 1 mol of benzoyl bromide to 1.5 moles of pyridine. The resulting solid addition compound was pulverized and to it 1 mol of benzaldehyde was added. An immediate reaction took place and the solid substance just described above was produced.

Phenyl-chloromethyl Benzoate and Pyridine, $C_5H_5NClCH(C_6H_5)OCOC_6H_5$. —On mixing equimolecular amounts of benzoyl chloride and benzaldehyde, an immediate reaction took place. When cold, the resulting oil was poured into one mol of pyridine. In about half an hour, the mixture had become a pasty solid. The solid material was filtered off and purified by dissolving in absolute alcohol and precipitating with dry ether. It then melted at 192° with decomposition.

Analyses. Subs., 0.6210, 0.5910: 18.67, 17.81 cc. of 0.1022 N AgNO₃. Calc. for $C_{19}H_{16}O_2NCl$: Cl, 10.90. Found: 10.90, 10.93.

A mixture of 10 g. (one mol) of benzoyl chloride and 5.6 g. (one mol) of pyridine was allowed to stand overnight. Only a few crystals had separated by that time. When 7.5 g. (one mol) of benzaldehyde was added, a reaction took place at once with the liberation of considerable heat. The solid product was purified as already mentioned by dissolving in absolute alcohol and precipitating with dry ether, and had the same m. p., 192°.

p - **Methoxyphenyl-bromomethyl** - p - **Nitrobenzoate and Pyridine,** C_5H_5NBrCH-$(C_6H_4OCH_3)(p)OCOC_6H_4NO_2(p)$. —$p$-Nitrobenzoyl bromide reacted with anisaldehyde to give a solid product in about 2 minutes. This material was pulverized and added in small amounts to an excess of pyridine. Complete solution took place, followed in a

[1] *Compt. rend.*, **31**, 113 (1850); *Ann.*, **154**, 347 (1870).

few minutes by the separation of a solid product.   This was purified by dissolving in absolute alcohol and precipitating with dry ether.   After drying *in vacuo* over sulfuric acid, the product melted at 126–128°.

Analyses. Subs., 0.6097: 13.55 cc. of 0.1022 N AgNO$_3$.   Calc. for C$_{20}$H$_{17}$O$_5$N$_2$Br: Br, 17.97.   Found: 18.17.

A semisolid product was obtained when the *o*-methylbenzoyl bromide and benzaldehyde were mixed and allowed to stand overnight.   This was added to one mol of pyridine, and the solid product thus obtained, after being purified by dissolving in absolute alcohol and precipitating with dry ether, melted at 206° with decomposition.

Analyses. Subs., 0.6630, 0.7751: 17.08, 19.91 cc. 0.1022 N AgNO$_3$.   Calc. for C$_{20}$H$_{18}$O$_2$NBr: Br, 20.83.   Found: 21.06, 21.00.

Reactions of Phenyl Bromomethyl Benzoate with Amines.

Phenyl Bromomethyl Benzoate and Methyl Amine.—A heavy white precipitate of methylamine hydrobromide began to form almost at once, when dry methylamine was passed into a solution of the phenyl-bromo-methyl benzoate in dry ether.   About 3 moles of the amine was added and the mixture then allowed to stand overnight. After filtering off the precipitate, the ether was evaporated and the oil obtained was separated into 2 fractions by distillation *in vacuo*.   The lower boiling fraction was redistilled under ordinary pressures, and proved to be benzylidene methylamine, b. p. 180–181°.   The higher boiling fraction solidified and was methyl benzamide, C$_6$H$_5$-CONHCH$_3$, m. p. 78–79°.

Phenyl-bromomethyl Benzoate and Diethylamine.—Phenyl-bromomethyl benzoate when treated with diethylamine in the manner just described under methylamine gave an oil, which, fractionated *in vacuo*, gave (1) boiling at 88° at 35 mm.; (II) boiling at 160–175° at 35 mm.   On redistillation under ordinary pressures, the 2 fractions were found to be benzaldehyde, boiling at 179–182°, and diethyl benzamide, boiling at 278–282°.

Phenyl-bromomethyl Benzoate and Trimethyl-amine, (CH$_3$)$_3$NBrCH(C$_6$H$_5$)-OCOC$_6$H$_5$.—When dry trimethyl-amine was passed into an absolute ether solution of phenyl-bromomethyl benzoate, a heavy white precipitate began to form at once.   When 3 moles of the amine had been added, the thick mass resulting was filtered and the solid recrystallized from alcohol.   It melted at 136–137°.

The white solid was completely soluble in water, and this solution when treated with sodium hydroxide gave off trimethyl-amine.   The odor of benzaldehyde could also be detected.   Acidification of the alkaline solution precipitated benzoic acid.

Analyses. Subs., 0.2632, 0.2042: AgBr, 0.1400, 0.1080.   Calc. for C$_{17}$H$_{20}$O$_2$NBr: Br, 22.85.   Found: 22.63, 22.50.

Phenyl-bromomethyl Benzoate and *o*-Chloro-aniline, C$_6$H$_5$CHBrNHC$_6$H$_4$Cl(*o*).—Phenyl-bromomethyl benzoate and *o*-chloro-aniline reacted immediately and produced a yellow solid.   By treatment with several portions of dry ether, the benzoic acid produced as a by-product was extracted.   The yellow solid remaining was analyzed.

Analyses. Subs., 0.5429: 17.84 cc. 0.1022 N AgNO$_3$.   Calc. for C$_{13}$H$_{11}$NBrCl: Br, 26.98.   Found: 26.86.

Some of this substance was treated with 20% sodium hydroxide solution, extracted with ether, and the ether extract dried over calcium chloride and evaporated.   The solid remaining was found to melt at 54°.   A mixed melting point with some benzylidene-*o*-chloroaniline (prepared from benzaldehyde and *o*-chloro-aniline) was taken and found to be 54°.

It was found that the yellow solid was completely hydrolyzed by water, so that if it were first dissolved in water and then sodium hydroxide solution added, *o*-chloroaniline was precipitated instead of benzylidene-*o*-chloro-aniline.

Phenyl-bromomethyl Benzoate and p-Chloro-aniline, $C_6H_5CHBrNHC_6H_4Cl(p)$.— Phenyl-bromomethyl benzoate and p-chloro-aniline were allowed to react, then treated as described under the o-chloro-aniline. Phenyl-bromomethyl-p-chloro-aniline was produced and yielded by treatment with 20% sodium hydroxide, benzylidene-p-chloro-aniline,[1] m. p. 62°.

Phenyl-bromomethyl Benzoate and p-Toluidine, $C_6H_5CHBrNHC_6H_4CH_3(p)$.— Phenyl-bromomethyl benzoate and p-toluidine reacted vigorously. After extraction of the benzoic acid with dry ether, the solid proved to be phenyl-bromomethyl-p-tolu-idine.

Analyses. Subs., 0.5949: 21.26 cc. 0.1022 N $AgNO_3$. Calc. for $C_{14}H_{14}NBr$: Br, 28.98. Found: 29.21.

Phenyl-bromomethyl Benzoate and Mono-ethylaniline.—A dry ether solution of phenyl-bromomethyl benzoate (one mol) was added to a dry ether solution of mono-ethyl aniline (two mol) and enough heat was generated to cause the ether to boil. After refluxing for 8 hours, the ether was decanted from the dark red viscous mass in the flask. The ether was extracted successively with sodium carbonate and dilute hydrochloric acid, which yielded benzoic acid and mono-ethylaniline respectively. Evaporation of the ether furnished a small amount of benzaldehyde.

Oxidation of the red viscous material with lead dioxide and hydrochloric acid yielded a green solution. An alcohol solution of the gummy material was red in direct light and green in reflected light. With mercuric chloride this solution produced a white precipitate which turned blue on drying. These properties correspond to those expected of the dye from diethyl-diamino-triphenyl carbinol.[2]

Phenyl-bromomethyl Benzoate and Diphenylamine.—When a dry ether solution of one mol of phenyl-bromo-methyl benzoate and a dry ether solution of two mols of diphenylamine were mixed, a colorless precipitate began to form almost at once. After standing for 1.5 hours a green gummy deposit formed. The solution was filtered, and the residue washed with ether. By using the method of Meldola,[3] crystals of the dye from diphenyl-diamino-triphenyl carbinol were obtained.

Phenyl-bromomethyl Benzoate and Dimethylaniline.—A dry ether solution of one mol of phenyl-bromomethyl benzoate and a dry ether solution of two mols of di-methylaniline were mixed and refluxed for 9 hours. A considerable amount of a green viscous mass separated. After evaporating the ether, the material was steam distilled. As much water as possible was then distilled off from the residue and an attempt was made to recrystallize the green mass remaining, but without success. The material was then reduced with zinc and hydrochloric acid and the leuco base of malachite green was obtained. On recrystallization from alcohol, this material melted at 92–93°.

Reactions of Phenyl-Bromomethyl Benzoate and Substituted Benzoates with Metals.

Phenyl-bromomethyl Benzoate and Zinc; Formation of Dibenzoyl-hydrobenzoin, $(C_6H_5CHOCOC_6H_5)_2$.—To an absolute ether solution of phenyl-bromomethyl benzoate (one mol) zinc dust (12 mol) was added in small portions. The flask was well shaken during the addition. The solution was then filtered and the zinc extracted twice with ether, then twice with hot benzene. Upon evaporation of the extraction liquors, the product, dibenzoyl-hydrobenzoin in 20% yields was obtained. It melted at 246–247°, after one crystallization from benzene.

On evaporation of the original ether solution, a tar was obtained which yielded

[1] *Ber.*, **34**, 829 (1901).
[2] *Ann. Spl.*, **3**, 363 (1865).
[3] *J. Chem. Soc.*, **41**, 192 (1882).

benzoic acid when extracted with 50% alcohol. Attempts to recrystallize the resin remaining were unsuccessful.

p-Bromophenyl-bromomethyl Benzoate and Zinc; Formation of Dibenzoyl-*p*,*p*-dibromo-hydrobenzoin, ((p)-BrC$_6$H$_4$CHOCOC$_6$H$_5$)$_2$.—An absolute ether solution of *p*-bromophenyl-bromomethyl benzoate was treated with a large excess of zinc dust in the same way as the phenyl-bromomethyl benzoate. A 16.8% yield of the dibenzoate, was obtained. After crystallization from benzene, the product melted at 225°.

Analyses. Subs., 0.0572: AgBr, 0.0368. Calc. for C$_{28}$H$_{20}$O$_4$Br$_2$: Br, 27.58. Found: 27.37.

Phenyl-bromomethyl Benzoate and Copper Powder.—The copper powder was prepared by adding zinc dust to a solution of copper sulfate. It was filtered off and digested with conc. hydrochloric acid, washed with water and dried *in vacuo* over sulfuric acid.

This reacted with the phenyl-bromomethyl benzoate in the same way as did the zinc dust, producing a 20% yield of the dibenzoate of hydrobenzoin.

With sodium, magnesium or aluminum powders, only negative results were obtained.

Phenyl-bromomethyl Benzoate and Alkalies or Alkali Cyanide.—The reaction between phenyl-bromomethyl benzoate and potassium hydroxide or potassium cyanide, although carried out under widely varying conditions, always produced complete hydrolysis.

Summary.

1. The reaction between aromatic acid halides and aromatic aldehydes is a general one. Benzoyl bromide, benzoyl chloride, and a number of their substitution products have been condensed with various aromatic aldehydes.

2. Halogen and nitro groups in either aromatic nucleus tend to retard the speed of reaction, and usually produce more stable substances. Methyl and methoxy groups tend to hasten the speed of the reaction, with the formation of less stable products.

3. The acid halide-aldehyde compounds react with pyridine or tertiary aliphatic amines to give stable addition products. These same products are produced by allowing the acid halide to react with pyridine and then adding the aldehyde.

4. The acid halide-aldehyde compounds react with primary and secondary aliphatic amines to give substituted benzamides, benzaldehyde, and the amine hydrobromides. With primary aromatic amines, the hydrobromides of benzylidene or substituted benzylidene anilines together with the aromatic acid are produced. Secondary and tertiary aromatic amines produce complex compounds in the triphenyl methane series.

5. The acid halide-aldehyde compounds react with zinc or copper to give esters of hydrobenzoin or substituted hydrobenzoin.

URBANA, ILL.