[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Reaction of Bromine with Silver Salts of Aromatic Acids[1]

BY RODERICK A. BARNES AND ROBERT J. PROCHASKA

The silver salts of most aliphatic acids react with bromine to produce satisfactory yields of the corresponding alkyl bromides.[2] Silver benzoate, the only aromatic salt which has been previously investigated, is reported to give 80%[3] and 14%[4] of bromobenzene. m-Bromobenzoic acid was the only other transformation product reported from this reaction.

We have investigated the reaction using a series of substituted benzoic acids and have found that the course of the reaction depends on the nature of the groups attached to the benzene ring. The experimental procedure used was essentially that of Luttringhaus and Schaede[4] in which bromine was added to a cold suspension of the dry silver salt and the reaction then completed by heating.

TABLE I

Silver salt of acid	Neutral product	Yield, %
Benzoic[a]	Bromobenzene	18
o-Chlorobenzoic	o-Chlorobromobenzene	38
m-Chlorobenzoic	m-Chlorobromobenzene	44
p-Chlorobenzoic	p-Chlorobromobenzene	55
o-Nitrobenzoic	o-Nitrobromobenzene	95
m-Nitrobenzoic	m-Nitrobromobenzene	89
p-Nitrobenzoic	p-Nitrobromobenzene	79
p-Anisic	2,4-Dibromoanisole	19–23
3-Bromo-4-methoxybenzoic	2,4-Dibromoanisole	92
p-Toluic	p-Bromotoluene[b]	17
β-Phenylpropionic	β-Phenylethyl bromide[c]	5
β-(p-Nitrophenyl)-propionic	β-(p-Nitrophenyl)-ethyl bromide	80
α,β-Diphenylpropionic	Stilbene dibromide	52
p-Nitrophenylacetic	p-Nitrobenzyl bromide	85

[a] Silver benzoate also reacted with iodine to produce 14% of iodobenzene but no iodide was formed from silver p-nitrobenzoate. [b] Silver p-toluate produced only traces of p-bromotoluene under the conditions used for the other salts; a modified procedure gave the yield reported. [c] High molecular weight neutral substances comprised about half the total product.

On the basis of a free radical mechanism for the reaction, a substituent on the benzene nucleus might influence the course of the reaction in two ways. First, by its effect on the rate of decarboxylation. An electron donating 4-substituent would increase the electron density at carbon one by virtue of the resonance
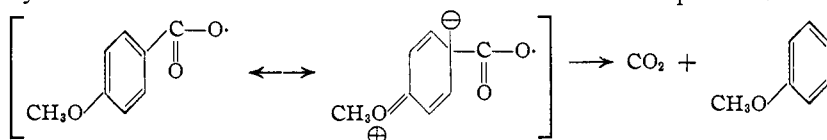
Thus, the carboxyl group could separate more readily with one of the bonding electrons. Sec-
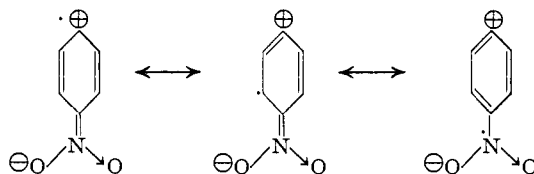
ond, the substituent would alter the stability of the aryl radical resulting after decarboxylation. An ortho or para substituent should stabilize this aryl free radical if extra resonance structures of the following kind make any appreciable contribution.

Our results show that these electronic effects are only of secondary importance in the aromatic series. Those salts which give a poor yield of the aryl bromide usually produce large amounts of brominated acids.[5] Therefore we believe that the reaction may follow either of two paths.
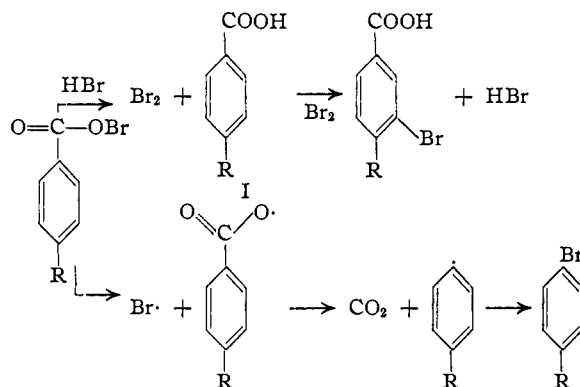
The critical factor is the ease of bromination of the free acid (I).[6] If this step is rapid, the hydrogen bromide produced converts more of the hypobromite to free acid and bromine.[3] Finally all of the hypobromite is decomposed before the desired reaction has taken place to any great extent. The yield of aryl bromide also depends to a considerable degree upon the temperature at which bromine is added to the silver salt. It is to be expected that the rates of the two competing processes vary with temperature to a different extent. This probably explains the discrepancy in yields of bromobenzene reported.[3,4] We have also found the yield of p-bromotoluene to be much

(1) Presented at the Atlantic City meeting of the Am. Chem. Soc., September 19, 1949.

(2) Kleinberg. Chem. Revs., 40, 381 (1947).

(3) Bockemüller and Hoffman, Ann., 519, 165 (1935).

(4) Luttringhaus and Schaede, Ber., 74, 1565 (1941).

(5) Silver anisate and silver p-toluate yield 73 and 66%, respectively, of 3-bromo-4-methoxybenzoic acid and 3-bromo-4-methyl-benzoic acid.

(6) Small amounts of free acid may be present as impurity in the silver salt or may be formed by reaction with moisture: $6RCOOAg + 3H_2O + 3Br_2 \longrightarrow 5AgBr + AgBrO_3 + 6RCOOH$.

greater when bromine was added slowly at the reflux temperature than by the usual procedure.

The ease of decarboxylation (in contrast to the extent of decarboxylation) for the 4-substituted benzoic acids varied as would be expected from the previous discussion. These acids are arranged in order of decreasing ease of decarboxylation based on qualitative observations.[7] The ob-

TABLE II

Acid	Substituent	σ
p-Anisic	$-OCH_3$	-0.268
p-Toluic	$-CH_3$	$-.170$
Benzoic	$-H$	$.000$
p-Chlorobenzoic	$-Cl$	$+.227$
p-Nitrobenzoic	$-NO_2$	$+.778$

served order is the same as that obtained by arranging the substituents in order of their electron donating abilities as measured by Hammett's σ function.[8] There is no direct relationship between the ease of decarboxylation and yields of aryl bromide. This is well illustrated by comparing 4-methoxy-3-bromobenzoic acid and o-nitrobenzoic acid which give approximately the same yield of aryl bromide but represent the two extremes[7] with respect to ease of decarboxylation.

By comparing the reaction of silver salts whose acids are brominated with equal ease we conclude that an increased electron density at the ring carbon is favorable for the desired process. Using Hammett's σ function[8] as a measure of the electron density in the nitro- and chlorobenzoic acids it is observed that as the electron density increases (σ decreases) the yield increases.[9]

TABLE III

| Substituent	σ	Yield, %
p-Nitro	0.778	79
m-Nitro	.710	89
o-Nitro	...	92
o-Chloro	...	38
m-Chloro	.373	44
p-Chloro	.227	55

For those acids in which a phenyl group is separated from the carboxyl by one or more carbon atoms, the introduction of a nitro group into the benzene nucleus greatly improves the yield (Table I). This is due in part to the reduction of nuclear bromination as in the benzoic acid series. We believe that a further important effect of the p-nitro group is to decrease the reactivity of the side chain toward attack by free radicals present

(7) Silver anisate and bromine evolved carbon dioxide rapidly in the cold while silver p-nitrobenzoate did not evolve noticeable amounts of carbon dioxide below the boiling point of the solution.

(8) Hammett, "Physical Organic Chemistry," McGraw–Hill Book Company, Inc., New York, N. Y., 1940, p. 188.

(9) In o-nitrobenzoic acid it is likely that steric inhibition of resonance of the nitro group with the nucleus results in an increased electron density at the ring carbon and hence the observed yield. In the chlorobenzoic acid series the inductive effect resulting in decreased electron density is at a maximum in the ortho position.

during the reaction.[10] The isolation of stilbene dibromide from the reaction of silver α,β-diphenylpropionate indicates that such attack actually does take place to a considerable extent in the absence of a p-nitro group. The large amount of polymeric neutral substance obtained from silver β-phenylpropionate can also be explained on this basis.
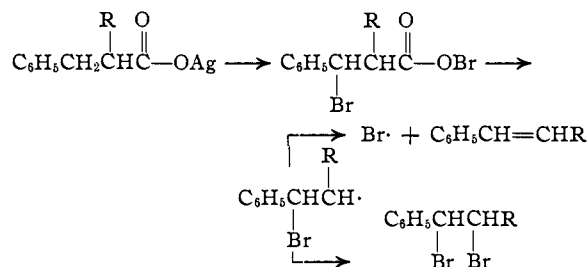
When R = H the olefin, styrene, polymerizes, but when R = C_6H_5- the reaction proceeds to the dibromide. An alternate explanation involving normal decarboxylation followed by further reaction of the bromide with free radicals seems unlikely since no polystyrene was produced when β-phenylethyl bromide was treated with N-bromosuccinimide or benzoyl peroxide in carbon tetrachloride solution.

The basic assumption that this reaction involves free radicals as intermediates is supported to some extent by the similarity between it and one in which benzoyl peroxide and bromine were heated and illuminated in carbon tetrachloride. Bromobenzene was formed in 38% yield (4% of chlorobenzene was also isolated). In this latter case it is certain that the free radicals which have been assumed for the silver salt reactions are actually present.[11] One of the characteristics of most free radical reactions is that the reactive intermediates are less specific than ionic intermediates and usually produce a variety of products including some from interaction with the solvent. This multiplicity of products has been noted in most of the experiments especially in such cases as silver o-chlorobenzoate where the yields of bromide are lower. One example, silver p-toluate, was carried out on a larger scale and the total product fractionated carefully.[12] Among the products which have been identified are bromotrichloromethane, p-chlorotoluene[13] and p-bromotoluene. A free radical mechanism is rather strongly sup-

(10) The abnormally slow reaction between p-nitrotoluene and N-bromosuccinimide to produce p-nitrobenzyl bromide (32%) is another example in which the p-nitro group inhibits the attack of a free radical at a methylene group adjacent to a benzene ring; Buu-Hoi, Ann., 556, 1 (1944).

(11) In this reaction benzoyl hypbromite may also be the intermediate and its decomposition need not necessarily involve free radicals.

(12) In most of the experiments our chief interest was to determine the yield of the expected bromide and no protracted effort was made to identify minor by-products.

(13) In a similar manner bromotrichloromethane and chlorobenzene have been isolated from the reaction with silver benzoate by Dauben and Tilles, THIS JOURNAL, 72, 3185 (1950).

ported by the isolation of bromotrichlorometh-
ane and aryl chlorides especially when considered
in conjunction with the fact that this mechanism
serves as a satisfactory basis for the correlation of
the results so far obtained.[14]

Experimental[15]

The silver salts were prepared by dissolving the acid in
one equivalent of 1% sodium hydroxide solution and adding
10% more than the theoretical quantity of silver nitrate
solution. The precipitate was filtered, washed well with
water, dried to constant weight at 100–105° and stored in
a desiccator over phosphorus pentoxide. The bromine
and carbon tetrachloride were dried over phosphorus pen-
toxide for several days before use. The following examples
illustrate the experimental procedure used. In each of
the examples listed in Table I the solid products were
characterized by a mixed melting point with an authentic
sample and the liquid products by physical constants or
preparation of a solid derivative.

p-Nitrobromobenzene.—Silver *p*-nitrobenzoate (34 g.)
was suspended in carbon tetrachloride (500 ml.) and bro-
mine (20 g.) was added dropwise at room temperature.
There was no visible reaction at room temperature. The
deep red solution obtained at the end of the addition was
heated slowly to the boiling point but there was no evolu-
tion of carbon dioxide below the reflux temperature.
The solution was boiled for three hours (during this time
the color gradually faded) and the hot solution filtered.
The filtrate was washed with sodium bisulfite and sodium
bicarbonate solutions. Acidification of the sodium bicar-
bonate extract produced 2 g. (10%) of recovered *p*-nitro-
benzoic acid. Evaporation of the carbon tetrachloride
left 20 g. (79%) of crystalline residue which melted at 126–
127° alone or when mixed with an authentic sample of *p*-
nitrobromobenzene.

2,4-Dibromoanisole.—Silver anisate (33 g.) was treated
with bromine (42.5 g.) as in the previous experiment.
There was an immediate evolution of carbon dioxide which
became turbulent as the solution warmed spontaneously to
40–50°. When this reaction had subsided the mixture
was refluxed three hours and processed as for the previous
experiment. The precipitate contained a considerable
quantity of acidic material mixed with the silver bromide.
This was extracted with boiling acetone. The total
weight of this acid was 23 g. (78%), m. p. 213–214°.[16]
Evaporation of the carbon tetrachloride left a residue of
6.6 g. (19%). The melting point of this solid was 61–
62°; there was no depression of the melting point by ad-
mixture with an authentic sample of 2,4-dibromoanisole.

p-Bromotoluene.—Bromine (83 g.) was added dropwise
(four hours) to a refluxing suspension of silver *p*-toluate
(126 g.) in carbon tetrachloride (1000 ml.). Only toward
the end of the addition did the solution become orange.
After refluxing for an additional hour the hot solution was
filtered and the precipitate washed with hot carbon tetra-
chloride. Chilling the filtrate caused the crystallization of
16.7 g. of 3-bromo-4-methylbenzoic acid, m. p. 201–202°.[17]
The sodium bicarbonate solution removed an additional
19.6 g. of material which was largely *p*-toluic acid, m. p.
160–165°. The carbon tetrachloride was distilled through
a column and the residue fractionated. Fraction one (0.8

g.) boiled at 103–105°, n^{22}D 1.5048, d^{20} = 1.987.[18] Frac-
tion two (1.1 g.) was collected from 160–168°, n^{22}D 1.5284.[19]
Oxidation of this fraction with potassium permanganate
solution produced an acid which was identified as *p*-chloro-
benzoic acid by conversion to its solid methyl ester with
diazomethane. The first crop of crystals obtained by
chilling a solution of the crude ester in petroleum ether
melted at 51.65° (methyl *p*-bromobenzoate, m. p. 81°,
was undoubtedly present). Treatment of the filtrate with
charcoal, filtration, and concentration of the solution pro-
duced nearly pure methyl *p*-chlorobenzoate, m. p. 42–44°.
There was no melting point depression with an authentic
sample of this ester.

Fraction three (16 g., 18%) was collected at 75–90° at
12 mm. This fraction solidified on cooling and melted
at 25–27°. Oxidation and methylation produced pure
methyl *p*-bromobenzoate, m. p. 80–81°. Fraction four
(7.5 g.) was collected from 120–140° at 12 mm., n^{22}D
1.5848. By oxidation, a portion of this fraction[20] was
converted to a mixture of acids melting at 140–180° which
was not investigated further. The residue was heated
up to 200° at 0.5 mm. but the only product obtained was
some *p*-toluic acid, m. p. 169–170°, which must have come
from decomposition of some product in the residue since
all acidic substances had been previously washed out with
sodium bicarbonate solution.

Bromobenzene.—A mixture of benzoyl peroxide (48.4
g.), bromine (32 g.) and carbon tetrachloride (400 ml.)
was illuminated with a 200-watt lamp and refluxed for
nine hours. The solution was washed with sodium bicar-
bonate solution which removed 6.8 g. of benzoic acid, m. p.
119–120°. The carbon tetrachloride was distilled off and
the residue fractionated. There was obtained 1.9 g.
(4.2%) of chlorobenzene, b. p. 133–136°, n^{22}D 1.5237.[21]
This sample was nitrated to yield 2,4-dinitrochlorobenzene,
m. p. 53.2–54°. The melting point of a mixture of this
product and a sample of pure 2,4-dinitrochlorobenzene
(m. p. 50.0–50.8°) was 52.0–52.8°. The melting point
of a mixture containing 91% of pure 2,4-dinitrochloroben-
zene and 9% pure dinitrobromobenzene was 52.0–53.0°.
Fraction two was collected at 151–154°, n^{22}D 1.5565.
This was identified as bromobenzene by nitration to pro-
duce 2,4-dinitrobromobenzene, m. p. 74–75°.

Reactions of β-Phenylethyl Bromide. A.—β-Phenyl-
ethyl bromide (34 g.), N-bromosuccinimide (45 g.), ben-
zoyl peroxide (1 g.) and carbon tetrachloride (300 ml.)
were refluxed for three hours. The solution was filtered
and the carbon tetrachloride evaporated. There was
obtained 30.5 g. (63%) of styrene dibromide. The liquid
remaining after removal of the styrene dibromide was dis-
tilled. Only an insignificant amount of non-volatile resi-
due remained.

B.—Benzoyl peroxide (3.5 g.), β-phenylethyl bromide
(20 g.) and silver bromide (1 g.) were refluxed for six
hours in carbon tetrachloride solution. Only a trace of
hydrogen bromide was evolved and 85% of the bromide
was recovered unchanged.

Summary

The silver salts of a number of substituted ben-
zoic acids have been converted to the correspond-
ing aryl bromides.

It has been shown that the competing reactions,
nuclear and side chain bromination can be mini-
mized by introduction of nitro groups into the
benzene nucleus.

(14) The results of Arcus, Campbell and Kenyon, *J. Chem. Soc.*,
1510 (1949), have been interpreted by them as essentially a displace-
ment reaction in which a bromonium ion is the attacking fragment.
We wish to suggest the possibility that a bromine atom could equally
well be the attacking fragment with the same steric result.

(15) All melting points are corrected.

(16) Salkowski, *Ber.*, **7**, 1013 (1874), reports the melting point of 3-
bromo-4-methoxybenzoic acid as 213–214°. The same melting point
is reported by Zincke, *Ann.*, **388**, 298 (1912), for 3,5-dibromo-4-
methoxybenzoic acid. The acid obtained above was proved to be
3-bromo-4-methoxybenzoic since its silver salt produced 2,4-di-
bromoanisole in 92% yield.

(17) Jannasch and Dieckmann, *ibid.*, **171**, 83 (1861), report a
melting point of 203.5–204° for this substance.

(18) Simons, Sloat and Meunier, THIS JOURNAL, **61**, 435 (1939),
report d^{20} 1.994, and Kharasch, Freiman and Urry, *J. Org. Chem.*,
13, 570 (1948), report $n^{19.2}$D 1.5060 for bromotrichloromethane.

(19) Gindraux, *Helv. Chim. Acta*, **12**, 925 (1929), reports *p*-chloro-
toluene to have n^{19}D 1.5223.

(20) This is probably a mixture of 2,4-dibromotoluene and 3,4-
dibromotoluene.

(21) Bruhl, *Ann.*, **200**, 187 (1879), reports chlorobenzene to have
n^{20}D 1.5248.

The observed results have been explained on the basis of a free radical mechanism and some evidence to support this view has been presented.

The Use of Amine and Phosphine Catalysts in the Preparation of Parathion[1]

BY A. D. F. TOY AND T. M. BECK

Introduction

Parathion (diethyl p-nitrophenyl thionophosphate) has been prepared by the reaction of diethyl chlorothionophosphate and anhydrous sodium p-nitrophenolate in chlorobenzene at 130°,[2,3] by the same reactants in a mutual solvent such as ethyl alcohol,[3] or by the reaction of diethyl chlorothionophosphate with an aqueous solution of sodium p-nitrophenolate.[3] The chlorobenzene process has the advantage of eventually giving a relatively high yield; however, the reaction itself takes an inconveniently long time in this medium. Cassaday and his co-workers[3] found that this reaction gave a 79% yield after 51 hours at 125°. The alcohol process, a rapid and convenient one, gives a yield of 75%, and the aqueous solution one of 64%.[3]

Without any diluent, diethyl chlorothionophosphate and anhydrous sodium p-nitrophenolate undergo a slightly exothermic reaction at about 150–160°. However, the process is difficult to control, and the product is contaminated with tarry impurities. The use of the dihydrate instead of the anhydrous salt in this reaction results in a vigorous hydrolysis of the chloride and the formation of no parathion. If chlorobenzene is present in the proportion of 250 ml. per gram mole of anhydrous sodium salt it was possible to reflux this mixture at 150–155°, at which temperature the reaction was substantially complete in three hours although partial isomerization of the product may have occurred.[4] Because of possible isomerization and the inconvenience of operating at this high a temperature and also because the more readily prepared sodium p-nitrophenolate dihydrate cannot be used under these conditions, it was felt that a means of accelerating this reaction at a lower temperature would be desirable.

Our discovery of a unique catalytic effect by certain amines indicated a means of bringing about the reaction under more favorable conditions. Preliminary studies[5] on triethylamine, tributylamine, N-ethylmorpholine, and hexamethylenetetramine showed that these compounds catalyze the reaction to varying degrees. This

(1) Presented at the meeting of the American Chemical Society, September 21, 1949, Atlantic City, N. J.

(2) Thurston, FIAT Final Report No. 949, October 14, 1946 (PB-60890).

(3) Fletcher, Hamilton, Hechenbleikner, Hoegberg, Sertl and Cassaday, THIS JOURNAL, **70**, 3943 (1948).

(4) Schrader, P. B. Report 95312 (1947).

(5) Toy and Beck, U. S. Patent 2,471,464 (1949).

work has since been extended to cover various types of amines and related compounds. The results are shown in Table I.

TABLE I

Catalyst	Mole %	Temp., °C.	Time, hr.	Yield, %	$n^{25}D$	Remarks
None		105	2	2.0	1.5461	b
Triethylamine	1.4	105	2	87.7	1.5387	
Triethylamine	0.7	105	2	89.3	1.5377	c
Diethylamine	1.4	105	2	17.3	1.5389	
Tri-n-butylamine	0.8	115	2	92.3	a	
N-Ethylmorpholine	1.0	110	2	88.1	a	
Triethanolamine	1.4	105	2	55.4	1.5371	d
Hexamethylene-tetramine	1.4	130	2.5	92.7	a	e
Dimethylaniline	1.4	105	4	88.4	1.5379	f
Trimethylamine	1.4	105	2	87.0	1.5374	
Pyridine	1.4	105	2	85.8	1.5380	
Benzyldimethyl-amine	1.4	105	2	82.8	1.5377	g
Phenyldiamyl-phosphine	1.4	105	2	89.3	1.5382	
Triethyl phosphite	1.4	105	2	10.8	1.5381	

^{a} Identity established by elementary analysis. ^{b} Product is highly impure. ^{c} Less vigorous reaction than preceding. ^{d} Appeared rather slow. ^{e} Appeared to be no reaction at 110°. ^{f} Reaction very slow. ^{g} Reaction very rapid.

The data in this table show clearly that maximum catalytic activity is limited to tertiary amines and phosphines. The ineffectiveness of diethylamine is without doubt the result of its immediate conversion to an amide. The poor results with triethanolamine can be explained by the fact that besides being a tertiary amine it is a primary alcohol capable of reacting with the chlorophosphate. While hexamethylene tetramine contains tertiary nitrogen atoms, it is chemically a condensed, deammoniated ammono-formaldehyde derivative. In general it will be noted that the best results were obtained with trimethylamine, triethylamine, tributylamine, N-ethylmorpholine, and phenyldiamylphosphine. Less satisfactory results were obtained with dimethylaniline. Triethanolamine was decidedly inferior, and both diethylamine and triethyl phosphite were almost ineffective. Benzyldimethylamine and, to a lesser extent, pyridine have the unusual effects of promoting rapid reaction while giving somewhat inferior yields. It may be significant in all these experiments that the yield falls short of 100% even after making a liberal allowance for losses in handling. It would appear that the catalyst promotes a competing reaction which uses up about 10% of the reactants.