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Pyrolysis of Silver *o*-Halobenzoates

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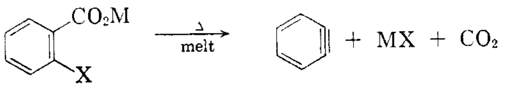
The pyrolysis of several metal salts of *o*-halobenzoic acids was studied. Silver *o*-chlorobenzoate pyrolyzed smoothly above its melting point to give phenyl *o*-chlorobenzoate, silver chloride, and carbon dioxide. Evidence is presented suggesting that benzyne, C_6H_4, may be an intermediate in the formation of the phenyl ester.

Dry pyrolyses of metal salts of carboxylic acids are generally complicated reactions which may result in the decarboxylative formation of ketones[1] and olefins.[2] Metal salts of simple aromatic acids frequently undergo extensive degradation when heated above their melting points.

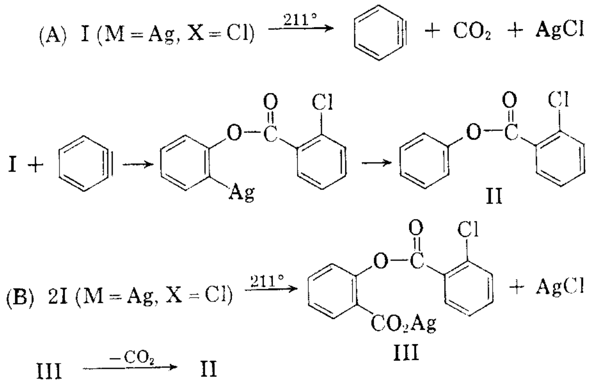
In the course of some studies in this laboratory aimed at new syntheses of benzyne,[3] the bulk pyrolysis of metal *o*-halobenzoates (I) was investigated briefly in an attempt to demonstrate Reaction 1.[4]



I (1)

Of the several salts that were examined, only the combination M = Ag and X = Cl gave results that suggested Reaction 1 could be realized.

Silver *o*-chlorobenzoate (I, M = Ag, X = Cl) melted at 211° *in vacuo* and underwent an exothermic reaction accompanied by the evolution of carbon dioxide and the formation of silver chloride. Phenyl *o*-chlorobenzoate (II) was isolated in 50.5% yield as the sole organic product. Two mechanisms for the formation of II are readily suggested:



In mechanism A, benzyne is presumably formed *via* a cyclic transition state with the near simultaneous loss of carbon dioxide and silver chloride. Phenyl *o*-chlorobenzoate results from a rapid reaction[5] of benzyne with undecomposed salt in the melt followed by hydrogen abstraction[6] to give II. In mechanism B, a metathetical coupling of two molecules of salt produces the ester III, which is decarboxylated in the melt to II.[6]

In order to test the latter hypothesis the ester-silver salt III was synthesized from *o*-chlorobenzoyl chloride and salicylic acid in pyridine followed by treatment of the ammonium salt of the resulting acid with silver nitrate. When a sample of authentic III was pyrolyzed under conditions identical with those used in the case of silver *o*-chlorobenzoate, a reaction occurred at approximately 200°. No liquid fraction was observed, and the product was a hard, black, insoluble mass. Extraction of this residue with ether afforded a trace of chlorobenzene as the only organic product. When the pyrolysis was carried out in the presence of a small amount of added silver chloride, similar results were obtained.

These results strongly suggest that III is not an intermediate in the pyrolysis of silver *o*-chlorobenzoate and that mechanism B is untenable. Although these observations in no sense prove the intermediacy of benzyne in the pyrolysis of I (M = Ag, X = Cl), some support is lent to mechanism A. Other paths to the observed product can be constructed but are difficult to rationalize. Since one of the benzene nuclei in the product, phenyl *o*-chlorobenzoate, is no longer bonded to either of its original substituents (carboxyl and chlorine) and since the pyrolysis occurs cleanly and in reasonable yield, the multistep paths to II which can be

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(1) R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry*, John Wiley & Sons, New York, N. Y., 1953, pp. 331-332.

(2) Unpublished observations in these laboratories. Also see O. Neunhoeffer and P. Paschke, *Ber.*, **72B**, 919 (1939).

(3) J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith, and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953).

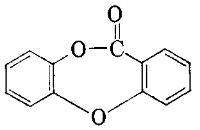
(4) The author is indebted to Prof. G. Wittig and Dr. G. Köbrich (Chemisches Institut der Universität, Heidelberg) for informing him of their work in this area prior to Dr. Köbrch's forthcoming publication.

(5) The nucleophilic addition of anions to benzyne at high temperatures is well known; see O. Kym, *J. prakt. Chem.*, **51**, 325 (1895); C. Haeussermann, *Ber.*, **32**, 1912 (1899); **33**, 939 (1900); **34**, 38 (1901). For a discussion of the mechanism of nucleophilic additions to benzyne, see J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Am. Chem. Soc.*, **78**, 601 (1956).

(6) The source of hydrogen is not clear but could be due to small amounts of water (see Experimental) in the salt or to degradative hydrogen abstraction from reactant or products.

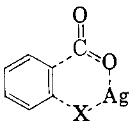
written involving free radical intermediates offer initially many conceptual difficulties.

When silver *o*-fluorobenzoate was pyrolyzed at its melting point (231°), a low yield of fluorobenzene was isolated. Silver *o*-bromobenzoate at 182° gave tars, while silver *o*-iodobenzoate underwent a vigorous reaction at 147°. From the latter experiment there was isolated a low yield of a colorless crystalline solid whose analysis, spectra, and properties are in accord with the previously unreported lactone of *o*-carboxy-*o*′-hydroxydiphenyl ether (IV).



IV

Possibly the difference in products observed in the pyrolyses of I (M = Ag, X = F, Cl, Br, I) is due to different timing in the collapse of a cyclic transition state, such as V.



V

The carbon-halogen bond energies decrease in the order C-F>C-Cl>C-Br>C-I. When X = F, transition states like V are most difficult to attain, and other reactions (*e.g.* decarboxylation) occur in preference to loss of silver fluoride. Experimentally carbon-fluorine bond rupture was not observed, and fluorobenzene was the only organic product isolated. When X = Cl, delocalization stabilization of transition state V is predominant, and collapse must occur with essentially simultaneous loss of carbon dioxide and silver chloride. When X = Br, I, silver bromide or iodide is probably expelled very easily before the benefit of the delocalized cyclic state V is manifested.[7]

Attempts were made to trap benzyne by pyrolyzing silver *o*-chlorobenzoate in the presence of addends. When pure furan and the anhydrous salt were heated alone in a bomb at 250°, high yields of benzoic acid were isolated and no other organic products were detected. At 175°, the same reactants gave only *o*-chlorobenzoic acid. Apparently under the strenuous reaction conditions, hydrogen abstraction from furan interferes with the normal course of reaction, for neither the expected Diels-Alder adduct[8] nor II was detected in the products. When the reaction with furan was run in benzene as solvent at 190°, only *o*-chlorobenzoic acid was isolated. Hydrogen abstraction also occurred in the presence of N-methylpyrrole, which gave fair yields of benzoic acid even at 190°. When an intimate mixture of silver *o*-chlorobenzoate and anthracene was pyrolyzed, no triptycene was detected among the products, which consisted mostly of phenyl *o*-chlorobenzoate.

A few other metal *o*-halobenzoates were pyrolyzed with unpromising results (Table I).

TABLE I

METAL *o*-HALOBENZOATES

I			
M	X	M.P., ° dec.	Remarks
Ag	F	231–232	See Experimental
Ag	Cl	211–212	See Experimental
Ag	Br	182–183	Isolated only tar on pyrolysis
Ag	I	147–148	See Experimental
Li	Cl	227	Stable at 300°
Cu/2	Cl	270–271	Isolated I (M = H, X = Cl) on pyrolysis
Hg/2	Cl	178–180	Stable at 300°

EXPERIMENTAL[9]

Preparation of metal o-halobenzoates. All of the silver salts employed in this work were prepared by suspending the pure carboxylic acid in distilled water and adding one equivalent of concd. ammonium hydroxide. The solution of the ammonium salt was filtered, and a solution of one equivalent of silver nitrate in distilled water was added slowly with vigorous stirring. The mixture was stirred for 30 min. and allowed to stand in the dark for 30 min. The silver salt was collected by suction filtration and was washed well with distilled water.

Lithium *o*-chlorobenzoate was prepared from the acid and lithium hydroxide in good yield.

Cupric and mercuric *o*-chlorobenzoate were prepared from the ammonium salt of the acid and cupric sulfate and mercuric chloride, respectively.

All of the salts were dried at 100° in a vacuum oven at reduced pressure. The silver salts of the *o*-halobenzoic acids gave satisfactory analyses, but the infrared spectra indicated traces of residual water which was difficult to remove.[6]

Pyrolysis of I (M = Ag, X = Cl). The dried salt I (47.2 g., 0.18 mole) was placed in a large sublimation tube with a solid carbon dioxide cold finger. The apparatus was evacuated to 0.05 mm. pressure and was heated externally in an oil bath. The salt began to melt at approximately 200°, and a vigorous reaction occurred with the evolution of carbon dioxide (in one run at 1 mm. the carbon dioxide was collected in a liquid nitrogen trap and was identified). A viscous liquid collected on the cold finger and the sides of the apparatus. The reaction subsided in a few minutes, and the tube was allowed to cool. The cold finger and the dark solid residue were extracted with ether, and the extracts were combined and washed successively with cold 1% hydrochloric acid and with water. The solvent was removed and the residue was distilled through a semimicro spinning-band column[10] to give 10.6 g. (50.5%) of pure phenyl *o*-chloro-

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(7) The occurrence of the aromatic ether linkage in IV is difficult to explain, and the low yields of this product make speculation unwarranted. Possibly IV arises from decarbonylation in the presence of silver salts of the cyclic bislactone of salicylic acid, a product not unexpected from the above considerations.

(8) G. Wittig and L. Pohmer, *Angew. Chem.*, **67**, 348 (1955).

(9) All melting points are corrected and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 21 double-beam infrared spectrometer equipped with sodium chloride optics (2–15 μ). Spectra were obtained on pure liquids or in potassium bromide wafers.

(10) R. G. Nester, *Anal. Chem.*, **28**, 278 (1956).

benzoate (II), b.p. 142–143° (1 mm.), n_D^{25} 1.5846. The distillation residue was negligible.

Anal. Calcd. for $C_{13}H_9ClO_2$: C, 67.11; H, 3.90; Cl, 15.24; mol. wt., 234. Found: C, 66.96; H, 4.27; Cl, 15.39; mol. wt., 245 (b.p. in benzene). The infrared spectrum showed ester carbonyl absorption at 5.73 μ. Basic hydrolysis of a small sample of the product gave *o*-chlorobenzoic acid (isolated) and phenol (identified as tribromophenol).

A sample of the dark solid obtained in the pyrolysis was shown by x-ray diffraction to contain large amounts of silver chloride.

An authentic sample of II was prepared in 67% yield from *o*-chlorobenzoyl chloride and phenol in dry pyridine. The pure ester had boiled at 125–127° (0.5 mm.), n_D^{25} 1.5843, and had a satisfactory analysis. The infrared spectrum of the authentic sample was identical with that of the pyrolysis product as isolated above.

Preparation of III. *o*-Chlorobenzoic acid (20.0 g., 0.13 mole) was converted to the acid chloride with 40 ml. of thionyl chloride. The acid chloride was added dropwise to a cooled (0°) and stirred solution of salicylic acid (17.7 g., 0.13 mole) in dry pyridine (60 ml.). The mixture was allowed to stand at 3° overnight and was then poured into a large excess of cold water. The solid was collected, washed with water, and sucked dry. Pure *o*-carboxyphenyl *o*-chlorobenzoate was obtained as colorless needles after one recrystallization from benzene, m.p. 169–170°. The yield was 12.4 g. (35%).

Anal. Calcd. for $C_{14}H_9ClO_4$: C, 60.77; H, 3.28. Found: C, 61.22; H, 3.51.

The recrystallized acid (12.4 g., 0.045 mole) was finely ground and suspended in 100 ml. of water. The mixture was stirred and cooled to 5° and was then slowly neutralized by the dropwise addition of one equivalent of concd. ammonium hydroxide. The cold solution was filtered into a beaker surrounded by an ice bath, and a cold solution of silver nitrate (7.6 g., 0.045 mole) in water (30 ml.) was added slowly with vigorous stirring. The thick, white salt that precipitated was stirred for an additional hour at 0° and was then collected by suction filtration. The salt was washed well with cold water and was dried. There was obtained 12.0 g. (69%) of pure III, m.p. 177–178° dec.

Anal. Calcd. for $C_{14}H_8AgClO_4$: Ag, 28.13. Found: Ag, 27.92.

Pyrolysis of III. Salt III (10.0 g., 0.03 mole) was pyrolyzed under conditions identical with those under which silver *o*-chlorobenzoate gave phenyl *o*-chlorobenzoate. Exothermic decomposition occurred at approximately 180°, and the temperature was raised to 225° over 3 hr. No volatile product appeared on the cold finger, and on cooling there was obtained approximately 8 g. of a black, hard, insoluble mass. The apparatus was washed out with ether, and the solid was pulverized and extracted with boiling ether. The combined ether solutions gave on concentration 0.3 g. of an oil which afforded a trace of chlorobenzene on distillation. No other volatile products could be distilled even at bath temperatures over 200° at 0.05 mm. The experiment was repeated with an intimate mixture of 10 g. of III and 0.5 g. of silver chloride. The results were substantially unchanged. In neither run could any II be detected.

Pyrolysis of I (M = Ag, X = F). The dried salt I (36.5 g., 0.15 mole) was pyrolyzed in bulk in the apparatus described for I (M = Ag, X = Cl). A vigorous reaction occurred slightly above the melting point of the salt, and the products were worked up as described above. Distillation of the liquid product afforded 4.0 g. of fluorobenzene, b.p. 85°, n_D^{25} 1.4657. A residue of less than 0.5 g. could not be distilled.

Pyrolysis of I (*M* = Ag, X = I). The dried salt I (34.1 g., 0.10 mole) was pyrolyzed in bulk in the apparatus described for I (M = Ag, X = Cl). A vigorous reaction occurred at approximately 150° and appeared to be complete in a few seconds. The solid products were worked up in the usual manner to give 3.2 g. (31%) of the lactone of *o*-carboxy-*o'*-hydroxydiphenyl ether, m.p. 180–181°, from benzene/pentane.

Anal. Calcd. for $C_{13}H_8O_3$: C, 73.58; H, 3.80. Found: C, 73.29; H, 3.76. The infrared spectrum showed a sharply split carbonyl absorption at 5.65, 5.70, and 5.75 μ. Scale molecular models predict a complex carbonyl spectrum on the basis of conformation considerations. The spectrum was free from hydroxyl absorption and showed no other characteristic functionality. Strong absorption at 13.70 μ suggested *o*-disubstituted phenyl.

Attempts to prepare an authentic sample of IV by the Baeyer-Villiger oxidation of xanthone with peracetic acid using sulfuric acid and *p*-toluenesulfonic acid catalysts failed, and in both cases xanthone was recovered unchanged after treatments of 1 week.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

The Reaction of Propylene Oxide, Styrene Oxide, and Cyclohexene Oxide with an Ivanov Reagent

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Propylene oxide reacted with the Ivanov reagent, the α-chloromagnesium derivative of the chloromagnesium salt of phenylacetic acid, to form α-phenyl-β-hydroxyvaleric acid and two stereoisomeric α-phenyl-β-methylbutyrolactones. From styrene oxide and the Ivanov reagent, two stereoisomeric α,γ-diphenyl-β-hydroxybutyric acids were obtained. Cyclohexene oxide and the Ivanov reagent reacted to form α-phenyl-α-(2-hydroxycyclohexyl)acetic acid.

Ethylene oxide has been found[3] to react with the α-chloromagnesium derivative of the sodium salt of phenylacetic acid (an Ivanov reagent) to produce α-phenyl-γ-hydroxybutyric acid.

This paper described the reactions of propylene oxide, styrene oxide, and cyclohexene oxide, re-

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[1] This paper represents part of a dissertation submitted by P. E. Wright for the Ph. D. degree in the University of Michigan.

[2] The Wm. S. Merrell Fellow.

[3] F. F. Blicke and H. Raffelson, *J. Am. Chem. Soc.*, **74**, 1730 (1952).