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The Pyrolysis of *o*-Halobenzoate Salts

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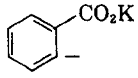
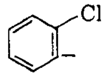
The thermal rearrangement of the dibasic potassium salt of phthalic acid to terephthalic acid has been postulated to proceed *via* the carbanion I.[1] Benzyne formation from chlorobenzene by treatment with base[2] or *o*-lithiofluorobenzene[3] can be rationalized by considering an incipient halocarbanion precursor such as II. We have attempted to obtain benzyne or its reaction products by the dry thermolysis of *o*-halobenzoate salts. A similar study has been recently reported by Köbrich.[4]



I



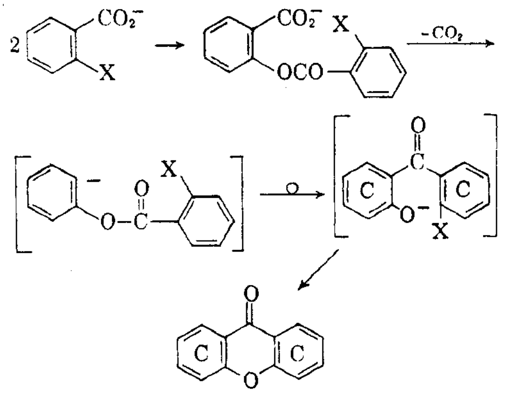
II

The alkali (lithium, sodium, and potassium) salts of *o*-halobenzoic acid (fluorine, chlorine and bromine) decompose smoothly at 325–380° *in vacuo* to produce 50–70% yields of xanthone. If either anhydrous silica gel or calcium oxide is finely admixed with these salts, decomposition to xanthone is drastically reduced and the parent acids can be regenerated in good yields from the pyrolysis residues. Xanthone formation, therefore, appears to be at least a bimolecular process in benzoate salt.

The main by-products of the pyrolysis give some clues as to the presence of benzyne in the reaction. If undehydrated calcium oxide is admixed with lithium *o*-fluorobenzoate, in addition to water and fluorobenzene (15%) an approximately 5% yield of phenol (as tribromide) is obtained in the cold trap. There was no evidence for the formation of triphenylene. Our attempts to treat the possible benzyne intermediate with anthracene also failed.[4]

If a mixture of the lithium salts of *o*-fluorobenzoic acid and benzoic acid is pyrolyzed, in addition to xanthone, phenyl benzoate (m.p. 65–67°; found: C, 78.7; H, 5.1) is isolated in 10% yield by alumina chromatography. Similarly a mixture of the lithium salts of *o*-bromobenzoic acid and 2-chloro-4-methylbenzoic acid produces at 400° a 14% yield of phenyl *p*-toluate (m.p. 75–76°; found: C, 79.5; H, 5.7). No phenyl benzoate is obtained. Under these conditions the yields of xanthone are greatly diminished. These phenyl esters do not necessarily arise *via* a reaction of the benzoate anion with benzyne, as potassium benzoyloxy benzoate undergoes decomposition at 350° to produce a mixture of phenyl benzoate (22%) and xanthone (8%). The salt of *o*-chlorobenzoyloxy benzoic acid could not be prepared; even under the mild conditions of stirring the acid in benzene in the presence of potassium at room temperature, the salt cleaves to potassium salicylate. Pyrolysis of mixtures of *o*-chlorobenzoyloxy benzoic acid and sodium carbonate or lithium hydroxide produced no xanthone.

There is, thus, no evidence that benzyne is an intermediate in the pyrolysis of *o*-halobenzoate salts. The pyrolysis can best be postulated as proceeding *via* an S_N2 displacement through the cyclic diester, disalicylide,[4,5] or a monoester such as:



EXPERIMENTAL

Alkali salts of o-halobenzoic acids. *o*-Fluorobenzoic acid was prepared by the permanganate oxidation of *o*-fluorotoluene.[6] *o*-Chlorobenzoic and *o*-bromobenzoic acids were commercial chemicals purified by vacuum sublimation. The salts were prepared by neutralizing the appropriate acid with a slightly less than equivalent amount of alkali hydroxide in methanol. The solvent was vacuum distilled and the salt residue extracted with ether. To test purity the salts were titrated potentiometrically.

o-Benzoyloxy benzoic acid was prepared from salicylic acid and benzoyl chloride,[7] mp. 126–127°. *o*-Chlorobenzoyloxybenzoic acid was similarly synthesized from salicylic acid and *o*-chlorobenzoyl chloride, m.p. 163–164°, yield 51%.

Anal. Calcd. for $C_{14}H_9O_4Cl$: C, 60.8; H, 3.3; neut. equiv. 277. Found: C, 61.2; H, 3.5; neut. equiv. 280. The salt from the chloro acid could not be prepared.

Pyrolysis. Pyrolyses were carried out *in vacuo* in a 50-ml. round bottom flask from which volatile materials were condensed in two traps placed in series, the first cooled with Dry Ice and the second with liquid nitrogen. Heat was supplied

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(1) F. Sorm and J. Ratusky, *Chem. and Ind.*, 294 (1958).

(2) J. Roberts, H. Simmons, L. Carlsmith, and C. Vaughan, *J. Am. Chem. Soc.*, **75**, 3291 (1953).

(3) G. Wittig, *Ang. Chem.*, **69**, 245 (1957).

(4) G. Köbrich, *Ber.*, **92**, 2985 (1959).

(5) K. Anshüte, *Ber.*, **52**, 1884 (1919).

(6) H. Clarke and E. Taylor, *Org. Syntheses*, Coll. Vol. II, 135 (1943).

(7) G. Einhorn, *Ber.*, **44**, 3310 (1911).

by a Wood's metal bath. The temperature of decomposition was taken from the time carbon dioxide was evolved. Concomittantly the volatile products including xanthone distilled from the reaction mixture. In the experiments with silica gel or calcium oxide very little carbon dioxide or distillable products were produced. Xanthone could be isolated in 9% yield from the distillate. Although some charring occurred in the reaction vessel, acid could be recovered by dissolving the residue in water, filtering, and acidifying.

The products were analyzed by separating the xanthone from the distillate mixtures with petroleum ether (b.p. 30–60°) in which it is insoluble. The petroleum ether solution after concentration was chromatographed with alumina.

Reaction with anthracene. Anthracene (20 g.) was intimately ground together with 15 g. of lithium *o*-fluorobenzoate and heated in an evacuated heavy wall Pyrex bomb tube at 400° for 15 min. After cooling the contents of the tube was extracted continuously with benzene. Evaporation of the solvent yields a solid mixture of only anthracene and xanthone (1 g.).

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The Relative Stabilities of *cis* and *trans* Isomers. X. The 1,3-Cyclohexanedicarboxylate Esters[1,2]

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Since the pioneering work of von Auwers,[3] organic chemists have been interested in the relationships between the stereochemical structures of compounds and their bulk physical properties such as density and boiling point. The Conformational Rule appears to be the pertinent relationship of widest applicability.[4,5] Exceptions to the rule are known, but rare, and it is instructive to seek the reasons behind such exceptions. Among hydrocarbons, the only pair of isomers known to the authors which do not follow the rule are the bicyclo[3,3,0]octanes.[6] The reasons for failure in this case are now understood,[7] and the Conformational Rule therefore is a reliable and useful method for assignment of geometrical structure to hydrocarbons.

Compounds containing functional groups present potentially more difficult systems to understand. Eliel and Haber[8] have shown that isomeric pairs of the various methylcyclohexanols follow the conformational rule (in terms of molecular volume), but the isomer with an equatorial hydroxyl always boils higher than the axial epimer. They have made the reasonable suggestion that this fact may be due to hydrogen bonding. Clearly, application of the rule for structural determination of compounds other than hydrocarbons can give only tentative conclusions until such interactions have been better delineated.

Apparent exceptions to the rule are the isomeric esters of 1,3-cyclohexane dicarboxylic acid.[9] The heats of combustion indicate a lower enthalpy for the *trans* isomer, and this is opposite what conformational analysis predicts. The difference is only of the order of experimental error though, and is almost certainly incorrect *a priori*. The refractive index and density of the *cis*-dimethyl ester are lower than the corresponding values for the *trans* compound, but the boiling point (at reduced pressure) is higher. With the diethyl esters, the *cis* isomer is reported to have the higher boiling point and refractive index, together with the lower density.

The present work was undertaken with the intention of confirming or denying the various relationships in physical properties reported by Skita and Rössler, as very powerful analytical methods which were not available to the earlier investigators could be brought to bear on the problem.

The geometrical structures of the acids are known with certainty, as the *cis* isomer forms an anhydride and the *trans* has been resolved.[10] Samples of the diastereomerically pure methyl esters were prepared by treating the corresponding pure acids with diazomethane. Vapor phase chromatography of these compounds with a column of silicone on firebrick showed each was pure, and contained less than 1% of the other isomer. The densities (and refractive indices) of these compounds are in agreement with the rule (Table I) and agree well with those reported by Skait and Rössler. Because of the well known difficulty of obtaining accurate boiling points at reduced pressure, the boiling points were measured at atmospheric pressure (752 mm.). It was was found that the *cis* isomer boiled higher than did the *trans* as reported.[9]

The conformational rule qualitatively (quantitatively under certain conditions[11]) relates the dif-

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(1) Paper IX, N. L. Allinger and S. Greenberg, *J. Org. Chem.*, **25**, 1399 (1960).

(2) This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation.

(3) K. von Auwers, *Ann.*, **420**, 84 (1920).

(4) N. L. Allinger, *J. Am. Chem. Soc.*, **79**, 3443 (1957).

(5) The rule states: "For stereoisomers in cyclic systems which do not differ in dipole moment, the isomer which has the smaller molecular volume is the isomer which has the higher heat content." It is usually true the isomer with the smaller molecular volume (higher density) is also the isomer of higher refractive index and higher boiling point, but the relationship is less dependable with these properties.

(6) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 436 (1935).

(7) Unpublished work by Dr. V. Zalkow.

(8) E. L. Eliel and R. G. Haber, *J. Org. Chem.*, **23**, 2041 (1958).

(9) A. Skita and R. Rössler, *Ber.*, **72**, 265 (1939).

(10) J. Boeseken and A. E. J. Peek, *Rec. Trav. Chim.*, **44**, 841 (1925).