modification suggested by Ichikawa,[3] in which the decomposition of the olefin-mercuric halide complex is rate determining, is definitely excluded by the repeated observations[3] that 2-alkoxyethylmercuric halides and 2-hydroxyethylmercuric halides give rise to unique rates. If the formation of the olefin–mercuric halide complex were fast and reversible a common rate would be observed (or at least a marked tendency of the rates to drift toward a common value as the reaction proceeds). If the formation of the olefin-mercuric halide complex is essentially irreversible, as suggested by Ichikawa, it is, by definition,[18] rate determining.

The observation that 2-acetoxyethylmercuric chloride is converted to 2-ethoxyethylmercuric chloride in ethanolic perchloric acid is mentioned by Ichikawa as evidence for the reversible formation of olefin–mercuric chloride π-complex. However, the facile solvolysis of 2-acetoxyethylmercuric iodide[17] makes it seem likely that this conversion simply proceeds *via* deoxymercuration to ethylene and mercuric chloride followed by readdition to the ethylene.

If the reaction scheme shown previously is correct, then the ratio k_3/k_2 is given by equation 10. It is

$$k_3/k_2 = [*_3]/[*_2][I^-] \qquad (10)$$

$*_n \equiv$ Transition state giving rise to k_n

identical in form and analogous in substance with the formation constant for a complex of a metallic ion with iodide ion. In this case, however, the central ion is the transition state containing only one iodine atom. In the same way k_4/k_3 is the formation constant for the transition state containing three iodine atoms from that containing only two. The former ratio, k_3/k_2, has a value, 3.2×10^3 l. mole^{-1}, and the later ratio, k_4/k_3, a value, 34 l. mole^{-1}. It is interesting to compare these with the various complexing constants of the mercuric ion. If the mercury were very weakly bound to the carbon skeleton in the transition state, so that the iodomercuric group resembled HgI^+ when only one iodine atom was present, the formation constants for the complexed transition states would be expected to resemble K_2 and K_3. On the other hand, if the mercury is firmly bound k_3/k_2 and k_4/k_3 might resemble K_3 and K_4, respectively. The values of K_2, K_3, and

$$K_2 = [HgI_2]/[HgI^+][I] \qquad (11)$$

$$K_3 = [HgI_3^-]/[HgI_2][I^-] \qquad (12)$$

$$K_4 = [HgI_4^-]/[HgI_3^-][I^-] \qquad (13)$$

K_4 are 10^{11}, 5×10^3, and 10^2,[16] supporting the hypothesis that the mercury is still firmly bound. This is consistent with the deoxymercuration transition state structure previously proposed,[7] in which the mercury is not being split away from the carbon skeleton in the rate-determining step.

Experimental

The preparation of solvents and acids have been previously described,[19] as has the kinetic method[6] and the preparation of 2-methoxyethylmercuric iodide.[20] The general method of Hofmann and Sand[21] was used to prepare 2-hydroxyethylmercuric iodide, m.p. 145° dec., lit.[21] 147°. The method of Ichikawa and coworkers[3] was used to prepare 2-isopropoxyethylmercuric chloride, m.p. 84.5–86°, lit.[3] 85–86°. Inorganic solutions were made up by weight from the best quality reagents commercially available.

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[18] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 99–100, 199–201.

[19] M. M. Kreevoy, *J. Am. Chem. Soc.*, **79**, 5929 (1957).

[20] M. M. Kreevoy and L. T. Ditsch, *J. Org. Chem.*, **25**, 134 (1960).

[21] K. A. Hofmann and J. Sand, *Ber.*, **33**, 1641 (1900).

Reactions of Aromatic Carboxylates. I. Evidence for the Intermediacy of Benzyne in the Pyrolyses of *o*-Halobenzoates[1]

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The formation of benzyne in the pyrolysis of *o*-halobenzoates has been demonstrated by trapping experiments with tetracyclone to form 1,2,3,4-tetraphenylnaphthalene. The intermediacy of benzyne in the formation of xanthone in alkali metal *o*-halobenzoate reactions has been shown by the isolation of two dichloroxanthone isomers in the pyrolysis of potassium 2,4-dichlorobenzoate. 3,4-Benzocoumarin has been found as the major product of the pyrolysis of potassium *o*-iodobenzoate and has been detected in other *o*-halobenzoate systems. The major reaction path can often be polymerization by intermolecular aromatic SN2 reaction and benzyne-type reactions can be suppressed by temperature control.

The dismaying violence and the unpredictable products of *o*-halobenzoate pyrolyses have done little to encourage their study until recent years when *o*-halobenzoates have been regarded as potential sources of benzyne.[2] The rationale behind these views[3–6] is that benzyne should be formed from *o*-halobenzoates by a decarboxylation and elimination of halide ion since benzyne is generated in an aromatic system by an initial carbanion formation with a subsequent elimination of a suitable *ortho* group. Attempts to form benzyne from carboxylates with an *ortho* diazonium group[7] and an *ortho* phenyliodonium group[8] have been successful. This paper is a presentation of results which demonstrate the presence of benzyne in the pyrolyses

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[1] Presented in part at the 141th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

[2] The following works are excellent reviews on benzyne: (a) R. Huisgen, "Organometallic Chemistry," H. Zeiss, Ed., Reinhhold Publishing Co., New York, N. Y., 1960, pp. 36–87; (b) J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961); (c) H. Heaney, *Chem. Rev.*, **62**, 81 (1962).

[3] G. Köbrich, *Ber.*, **92**, 2985 (1959).

[4] H. E. Simmons, *J. Org. Chem.*, **25**, 691 (1960).

[5] J. K. Kochi, *ibid.*, **26**, 932 (1961).

[6] G. Köbrich, *Angew. Chem.*, **74**, 428 (1962).

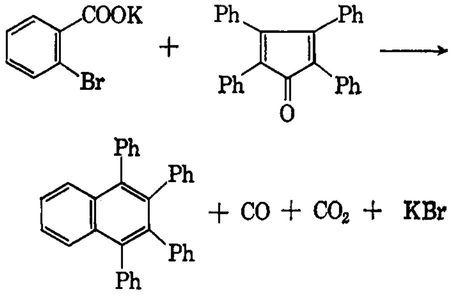
[7] M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **82**, 3802 (1960).

[8] E. LeGoff, *ibid.*, **84**, 3786 (1962).

of *o*-halobenzoates and help to define the limits of benzyne-type reactions in these systems.

Simmons[4] found that silver *o*-chlorobenzoate gave a 50% yield of phenyl *o*-chlorobenzoate upon pyrolysis at 212°. A postulated intermediate for an S_N2, decarboxylation and proton abstraction route, the silver salt of *o*-(*o*-chlorobenzyloxy)benzoic acid, did not afford phenyl *o*-chlorobenzoate under similar conditions. Supplementing this observation is a recent finding of Köbrich[6] that silver 2-chloro-4-methyl benzoate pyrolyzes to a mixture of *m*- and *p*-cresol esters. Neither of these arguments for the intermediacy of benzyne are fortified with successful attempts to trap benzyne with anthracene, furan, or tetracyclone. A conclusive proof for benzyne would consist of trapping with dienophiles and isolating products of cine-substitution with the appropriate reservations outlined by Heaney.[2c]

Benzyne Trapping.—At the outset of this work, attempts to trap benzyne with anthracene met with the same negative findings as reported by Simmons[4] and Kochi[5] except that a mass spectrum of ether soubles from an *o*-bromobenzoate–anthracene reaction had large peaks at 178 (anthracene), 196 (xanthone), and 254 (possible triptycene). This result encouraged further efforts. Tetracyclone proved to be a suitable dienophile trap for the intermediate benzyne. When potassium *o*-bromobenzoate was heated to 300–315° for five minutes in a nitrogen atmosphere with tetracyclone, 1,2,3,4-tetraphenylnaphthalene was formed (eq. 1). The yields, based on bromobenzoate, ranged from 3.4 to 8.2%. The product gave no melting point depression with an authentic sample[9] and their infrared spectra were superimposable.

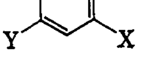


(1)

Other *o*-halobenzoates gave tetraphenylnaphthalene when treated in similar fashion. These results are listed in Table I.

TABLE I

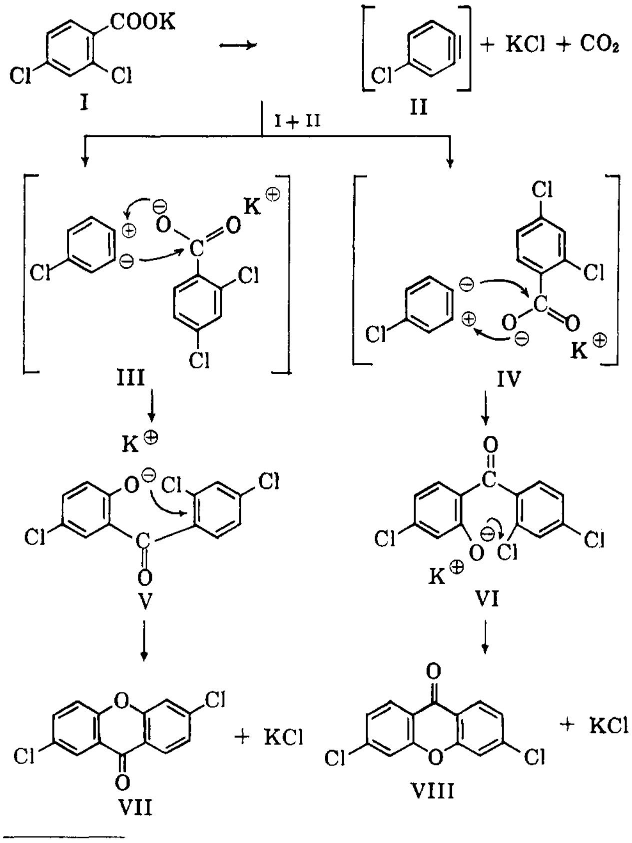
PYROLYSES OF *o*-HALOBENZOATES IN THE PRESENCE OF TETRACYCLONE



M	X	Y	Yield of tetraphenylnaphthalene, %
K	Br	H	8.2
Cs	Br	H	11.7
K	I	H	4.8
Ag	Cl	H	0.5
Na	Cl	H	6.1
Cs	Cl	Cl	10.5

Benzyne and Xanthone Formation.—In the pyrolysis of alkali metal *o*-halobenzoates, xanthone is usually the major product. This reaction was first reported by Richter in 1883[10] for sodium *o*-chlorobenzoate. Some forty years later xanthone was an unexpected product of the pyrolysis of calcium *o*-chlorobenzoate in 18% yield.[11] Recently Kochi[5] reported yields as high as 70% for xanthone formation from alkali metal *o*-halobenzoates, but maintained that benzyne was not an intermediate.

One of the principal conclusions of this work is that benzyne is an intermediate in xanthone formation. The basis for this statement is the isolation of two xanthones from the pyrolysis of a substituted *o*-halobenzoate. When potassium 2,4-dichlorobenzoate was heated between 300° and 309° for thirty minutes under a nitrogen atmosphere, two dichloroxanthones were formed in 33% yield and 41% selectivity. The only ester isolated from this reaction was *m*-chlorophenyl 2,4-dichlorobenzoate in 10% yield. The two isomeric ketones were present in about 1:1 ratio and were separated by column chromatography. The 3,6-dichloroxanthone isomer (VIII) had the melting point 183–184°.[12] The 2,6-dichloroxanthone isomer (VII) melted at 216–216.5° and matched the product of an independent synthesis. The proof of structure of this latter compound stems from the reaction of potassium 2,4-dichlorobenzoate and potassium *p*-chlorophenolate in hot nitrobenzene with an Ullmann–Goldberg catalyst (Cu/CuCl)[13] to effect *ortho* displacement. Ring cyclization of the resulting derived acids with acetic anhydride and sulfuric acid gave a nonacidic material



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(9) G. Wittig and E. Knauss, *Ber.*, **91**, 906 (1958).

(10) R. Richter, *J. prakt. Chem.*, [2] **28**, 273 (1833).

(11) W. Lawson, W. H. Perkin, Jr., and R. Robinson, *J. Chem. Soc.*, **125**, 624 (1924).

(12) M. Julia and G. Tchernoff, *Bull. soc. chim. France*, 546 (1952).

(13) A. A. Goldberg and A. H. Wragg, *J. Chem. Soc.*, 4227 (1958).

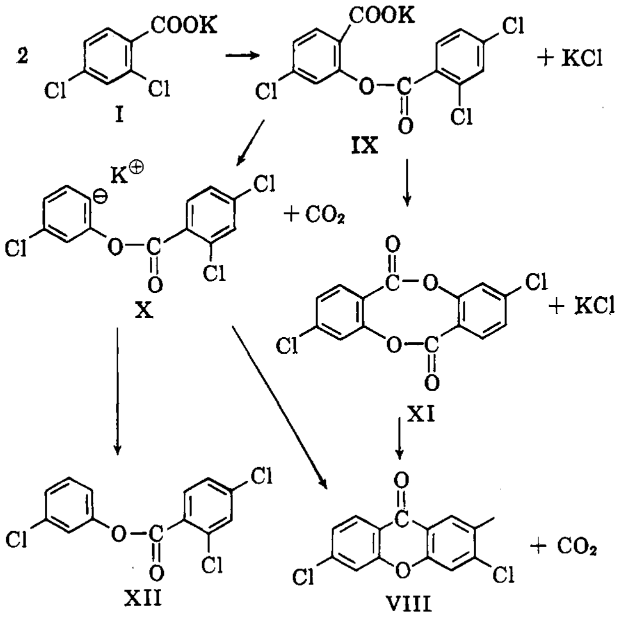
which, after crystallization from ethanol, melted at 215–216° and displayed the same infrared spectrum as the material from the pyrolysis reaction. A mixture melting point of these two products gave no depression.

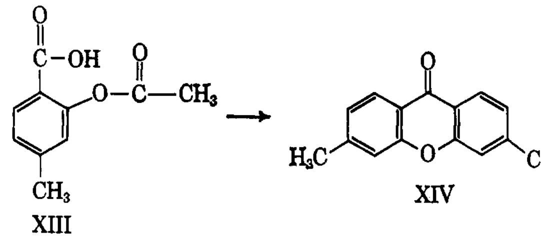
Two dichloroxanthones are predicted by a benzyne-type reaction. In this mode of reaction chlorobenzyne II is generated and attacked by another 2,4-dichlorobenzoate molecule. A concerted addition of benzoate to benzyne gives a phenolate system which precedes an unexceptional displacement for the xanthone ring closure (VII and VIII). (See p. 3189, col. 2.)

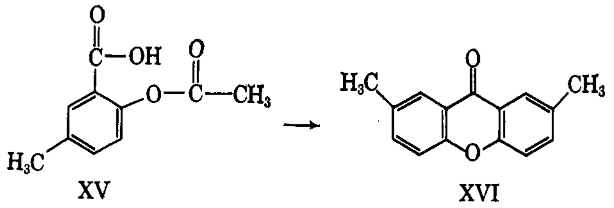
Careful examination of all chromatographic cuts of esters in the potassium 2,4-dichlorobenzoate reaction gave no evidence for the presence of *p*-chlorophenyl 2,4-dichlorobenzoate. Only the *meta* isomer was formed. Both isomers would be predicted to occur if I added nonconcertedly to II to give intermediates such as X which could protonate to give an ester such as XII. Consequently, concertedness in the addition of I to II is suggested, but is not proven. To examine this point further, potassium 2-(2,4-dichlorobenzoyloxy)-5-chlorobenzoate was heated to 310°. The principal product was *p*-chlorophenyl 2,4-dichlorobenzoate. No dichloroxanthones were detected. Since the intermediate anion resulting from decarboxylation of this salt would be the same as one derived from the nonconcerted addition of I to II, concertedness in the dichloroxanthone reaction route is implied strongly. In addition to being evidence against the *cis*-disalicylide route and its variant (*vide infra*), this experiment permits the conclusion that *m*-chlorophenyl-2,4-dichlorobenzoate was not formed in the 2,4-dichlorobenzoate pyrolysis by a benzyne intermediate, but arose from an S_N2 reaction on the *o*-chloro group, followed by decarboxylation and proton abstraction (IX → X → XII).

An example of nonconcerted addition of benzoate to benzyne is that of silver 2,4-dichlorobenzoate wherein no xanthone isomers were detected; both chlorophenyl esters were formed. This difference in the potassium and silver experiments lies probably in the nature of the metal carboxylate bond, which dictates the site requirements of attack by the benzyne.

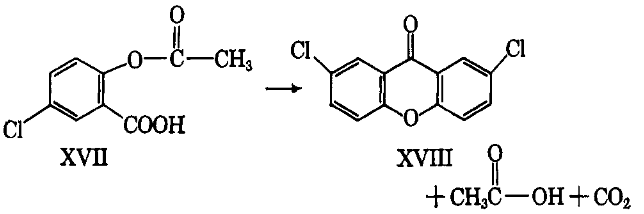
A possible route for xanthone formation involves a double displacement of halogen to form a *cis*-disalicylide (XI), which is reported to decarboxylate to xanthone.[14] In those reactions known to go to xanthones through a *cis*-disalicylide route, only one disubstituted isomer of xanthone is formed. Examples of this effect are the formation of 4,5-dimethylxanthone from *o*-cresyl-*o*-cresotinate,[15] 3,6-dimethylxanthone (XIV) from *o*-acetyl-*m*-cresotic acid (XIII), and 2,7-dimethylxanthone (XVI) from *o*-acetyl-*p*-cresotic acid (XV).[16]







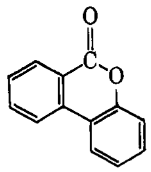
We have found that only one xanthone isomer, 2,7-dichloroxanthone (XVIII), is formed in the pyrolysis of 5-chloroacetylsalicylic acid (XVII). Consequently,



the *cis*-disalicylide route does not obtain in the pyrolysis of potassium 2,4-dichlorobenzoate.

A variant of this mechanism involves the initial S_N2 product IX which decarboxylates to anion X capable of rearranging to a xanthone VIII *via* an intermediate phenolate.[5] This path is untenable since it also predicts only one isomer, 3,6-dichloroxanthone, in the 2,4-dichlorobenzoate system.

3,4-Benzocoumarin Formation.—When the xanthone reaction was extended, to potassium *o*-iodobenzoate, the yield of xanthone dropped sharply, and an ester was isolated as the main ether-soluble product. The ester was shown to be 3,4-benzocoumarin (XIX) or the δ-lactone of 2′-hydroxydiphenyl-2-carboxylic acid. Yields ranged from 18% to 33%. This ester was also formed in 3.3% yield during a potassium *o*-bromobenzoate pyrolysis carried out under 255-p.s.i. carbon dioxide. Examina-



XIX

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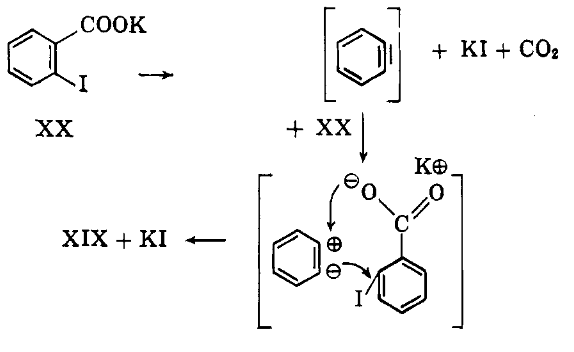
[14] R. Anschutz, *Ber.*, **52**, 1884 (1919).

[15] M. Schopf, *ibid.*, **25**, 8645 (1892).

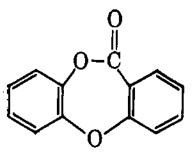
[16] L. Anschutz and G. Gross, *ibid.*, **77**, 647 (1944).

tion of its reaction path was assisted by the pyrolysis of potassium *o*-(*o*-iodobenzoyloxy)benzoate at 240°. The chief product was phenyl *o*-iodobenzoate although 3,4-benzocoumarin and xanthone were formed. Since this salt cannot be the principal intermediate in the *o*-iodobenzoate reaction, a concerted addition—displacement to 3,4-benzocoumarin as well as the addition—rearrangement to xanthone would seem to be feasible.



3,4-Benzocoumarin does not rearrange to xanthone under the reaction conditions. This finding rules out a long-standing contention[17] that it was an intermediate in the formation of xanthone from phenyl salicylate.

Silver *o*-Iodobenzoate.—One of the more interesting aspects of *o*-halobenzoate reactions is the report of Simmons[4] that during silver *o*-iodobenzoate pyrolysis there is formed a compound that melts at 180–181° and has infrared absorption at 5.65, 5.70, and 5.75 μ. On the basis of the infrared and elemental analyses, the compound was designated as the lactone of *o*-carboxy-*o*′-hydroxydiphenyl ether. Although no material melting at 180–181° was isolated in our experiments, it is unlikely that the structure assignment is correct for the following reasons.



XXI

(1) Structure XXI recently has been prepared by Lewis[18] from 2′-hydroxy-2-phenoxybenzoic acid by lactonization and from *o*-phenyloxybenzoic acid by oxidative coupling. Its melting point is given at 66–69°.

(2) The infrared spectra of depsidones, such as vicanicin, substances known to have the nucleus of XXI, display one carbonyl absorption[19] (5.75 μ).

In our hands, silver *o*-iodobenzoate was pyrolyzed in a nitrogen atmosphere to 3,4-benzocoumarin (10%), xanthone (5%), phenyl *o*-iodobenzoate (5%), phenyl benzoate (10%), and diphenic anhydride (5%).

Nonhalogenated Esters.—One of the esters formed in the pyrolysis of *o*-halobenzoates is phenyl benzoate. This type of product was first mentioned by Kochi[5] for a mixture of lithium *o*-bromobenzoate and lithium 2-chloro-4-methyl benzoate which, after heating to 400°, gave phenyl *p*-toluate. A nonhalogenated ester, *m*-cresyl-*p*-toluate, was formed by the pyrolysis of potassium 2-chloro-4-methyl benzoate.[6] It is possible that these nonhalogenated esters are formed from the expected phenyl *o*-halobenzoates by dehydrohalogenation involving the hydrogen evolved by the charring process. Phenyl benzoate was formed in 3.2% yield during an explosive reaction of potassium *o*-bromobenzoate as well as during a violent silver *o*-iodobenzoate pyrolysis. When the potassium *o*-bromobenzoate reaction was run at a temperature of 300–315° with a carbon dioxide pressure of 100 p.s.i., the yield of phenyl benzoate fell to 0.66%. A mass spectrum of the bomb reaction gases showed 0.4% hydrogen.

Acid–Salt Reaction.—When the pyrolysis of potassium *o*-bromobenzoate was carried out in the presence of *o*-bromobenzoic acid, phenyl *o*-bromobenzoate was obtained in yields of 37 to 46%. The possibility that this proceeds through an SN2 product, *o*-(*o*-bromobenzoyloxy)benzoic acid, is diminished by the observation that the latter acid, under the same reaction conditions, affords a 5.1% yield of phenyl *o*-bromobenzoate. The finding supports, but does not prove, that the ester was formed by concerted addition of the acid to benzene derived from *o*-bromobenzoate.

Polymers.—The formation of polysalicylates by an intermolecular SN2 reaction of the carboxylate on halogen takes place to a considerable degree. To be sure, it accounts for most of the reaction products in certain cases, particularly if the temperature is maintained below that necessary for decarboxylation. When silver *o*-iodobenzoate was heated under vacuum (20 mm.) for one hour between 175–200°, the major portion (88%) of the reaction products was a chloroform-soluble oligomer with a number of average molecular weight of 3150. Similarly, potassium *o*-bromobenzoate afforded an oligomer (molecular weight, 2200) representing 76% of the reaction products by maintaining the temperature at 240° for 30 minutes. The polymer run gave off very little carbon dioxide, whereas maintaining the temperature at 300° gave a quantitative yield (based on the xanthone reaction) of carbon dioxide.

Experimental[20]

Apparatus.—The apparatus for the pyrolytic experiments, unless otherwise noted, consisted of a 25- or 50-ml. reaction flask fitted with two Claisen adapters for gas inlet and a thermocouple lead. An exit tube led to a trap and a 1-in. head of mercury. The system was evacuated and flushed with nitrogen at least five times prior to immersion in a Wood's metal bath. The bath was heated by a Hoskins furnace. All reactions were run with a nitrogen sweep and reaction mixtures were maintained under nitrogen until their internal temperature was 35–40°.

Preparation of Salts.—Salts of the *o*-halobenzoates were prepared by reaction of stoichiometric quantities of acid and potassium hydroxide in water. After removal of water, the salts were washed with ether and dried for 24 hr. at 100° (0.5 mm.) in an Abderhalden pistol. Nujol infrared spectra were taken to ensure removal of water and parent acids.

Potassium 2,4-Dichlorobenzoate.—Potassium 2,4-dichlorobenzoate (4.58 g.) was heated above 300° for 30 min. under a nitrogen atmosphere. The temperature never exceeded 309°. The reaction mixture was a frothing red melt. After cooling, the reaction mass was washed with ether, acetone, and benzene. The washings were combined and stripped to give a residue weighing 1.655 g. The salt material of the reaction was dissolved in water and acidified. A 0.91 g. sample of 2,4-dichlorobenzoic acid was collected. Chromatography on acid-washed alumina

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(17) E. Strohbach, *Ber.*, **34**, 4136 (1901).

(18) J. R. Lewis, *J. Chem. Soc.*, 2533 (1962).

(19) S. Nulakantan, T. R. Seshandri, and S. S. Subramanian, *Tetrahedron Letters*, **18**, 597 (1962).

(20) Melting points are uncorrected. Elemental analyses were done by Mr. James Stiles of these laboratories.

with benzene as the eluent gave 275 mg. of material with an ester infrared spectrum in the fore fraction. Two crystallizations from ethanol gave white crystals, m.p. 98.5–99.0°, of *m*-chlorophenyl 2,4-dichlorobenzoate.

Anal. Calcd. for $C_{13}H_7Cl_3O_2$: C, 51.77; H, 2.34; Cl, 35.27. Found: C, 51.67; H, 2.56; Cl, 35.75.

This ester was hydrolyzed to *m*-chlorophenol and 2,4-dichlorobenzoic acid.

The second fraction of the benzene eluent contained a white solid, which melted at 216–216.5° after crystallization from ethanol.

Anal. Calcd. for $C_{13}H_6Cl_2O_2$: C, 58.89; H, 2.28. Found C, 58.63; H, 2.38.

This dichloro ketone was 2,6-dichloroxanthone. Immediately after this fraction came another ketonic material, 3,6-dichloroxanthone. One crystallization of the second ketone gave white crystals melting at 183–184°. Infrared spectra distinguished between the two isomers in the fingerprint region. The 3,6-dichloroxanthone had strong bands (chloroform), 9.38, 10.50, 11.59, and 11.85 μ; whereas, the 2,6-isomer had only one strong band at 10.85 μ. The total weight of dichloroxanthones was 651.6 mg. for a 33% yield and 41% selectivity. The 2,6-isomer fraction weighed 275 mg; the 3,6-isomer fraction weighed 175 mg.; 150 mg. of dichloroxanthones was a mixture of the two isomers. Another 315 mg. came off the column with more polar solvents. The latter were not characterized.

Preparation of 2,6-Dichloroxanthone.—Potassium 2,4-dichlorobenzoate (1.202 g.) and potassium *p*-chlorophenolate (0.949 g.) were heated with copper powder (0.0406 g.) and cuprous chloride (0.0904 g.) in 10 ml. of refluxing nitrobenzene for 20 min. The products were washed with ether, dissolved in dilute base and filtered. Acidification was followed by ether extraction. The acidic ether residue was treated with 5% sodium bicarbonate and re-extracted. Another acidification of the bicarbonate solution gave 566 mg. of a light brown precipitate. This was dissolved in 10 ml. acetic anhydride containing 5 microdrops of concentrated sulfuric acid. After 45 min., the mixture was poured into chilled 5% sodium hydroxide. The precipitate was collected, washed with base followed by water, and dried. It weighed 146 mg. and possessed the same infrared spectrum as the dichloroxanthone (m.p. 216–216.5°) from the 2,4-dichlorobenzoate pyrolysis. Recrystallization from ethanol gave a melting point of 215.5–216.5°. A mixture melting point determination of the two samples showed no depression.

Potassium *o*-Bromobenzoate.—Potassium *o*-bromobenzoate (2.725 g.) was heated to 324° for 5 min. in a nitrogen atmosphere. At the end of this time the mass exploded. The ether-soluble material weighed 788 mg. and were chromatographed on alumina to give 375 mg. of xanthone. Analysis was made by infrared comparison and mixture melting point determination with that of authentic material. The yield was 33.6%.

Potassium *o*-Bromobenzoate (Pressure).—Potassium *o*-bromobenzoate (4.78 g.) was placed in a 300-ml. Aminco bomb under 100-p.s.i. carbon dioxide and heated to 300–312° for 15 min. The maximum pressure was 255 p.s.i.; the final bomb pressure was 162 p.s.i. The mass spectrum of the final gas indicated the presence of 0.4% hydrogen. Acid-washed alumina chromatography separated the nonsalt products as follows: phenyl benzoate (0.55%), xanthone (12.5%), and 3,4-benzocoumarin (3.3%). Analyses were carried out by infrared and vapor phase chromatography. Unidentified oils brought off the column by polar solvents totaled 61% of the total material obtained from the column and had the infrared spectrum of an ester and a ketone.

Potassium *o*-Bromobenzoate (Low Temperature).—Potassium *o*-bromobenzoate (2.380 g.) was heated in a nitrogen atmosphere to 240° for 30 min. Only 8.9 mg. of carbon dioxide was evolved. Ether soluble material of the reaction mixture weighed 0.135 g. and had the infrared spectrum of a mixture of xanthone and phenyl *o*-bromobenzoate. Chloroform soluble material weighed 0.440 g. and had the infrared carbonyl absorption at 5.72 μ. The latter oil was coagulated with chloroform and methanol. Unchanged salt was recovered and converted to 0.895 g. of *o*-bromobenzoic acid. The molecular weight of the coagulate was 2200.

***o*-Bromobenzoate–Anthracene.**—Potassium *o*-bromobenzoate (3.228 g.) and anthracene (0.602 g.) were heated between 300 and 325° for 40 min. in a nitrogen atmosphere. The reaction mixture was treated with ether. The ether-soluble material was chromatographed. No triptycene was separated. A mass spectrum of the ether-soluble material had three large peaks at 178 (7200), 196 (3380), and 254 (158). They correspond, respectively, to anthracene, xanthone, and triptycene.

Preparation of 1,2,3,4-Tetraphenylnaphthalene from Potassium *o*-Bromobenzoate.—Potassium *o*-bromobenzoate (3.22 g.) was added slowly in a nitrogen atmosphere to molten tetracyclone (4.2 g.) at 305° for 20 min. The benzene-soluble products were chromatographed on acid-washed alumina. A petroleum ether–benzene eluent (90/10) brought down 0.327 g. of a clear oil which was crystallized with methanol, m.p. 204.5–205.0°. Its melting point was undepressed when mixed with authentic 1,2,3,4-tetraphenylnaphthalene,[9] and its infrared spectrum was superimposable on that of authentic material.

Anal. Calcd. for $C_{34}H_{24}$: C, 94.41; H, 5.59. Found: C, 94.19; H, 5.97.

Silver *o*-Chlorobenzoate and Tetracyclone.—Silver *o*-chlorobenzoate (2.89 g.) and tetracyclone (3.84 g.) were mixed and heated to 210–220° in a nitrogen atmosphere for 1 hr. The reaction products that were benzene-soluble were chromatographed on acid-washed alumina. Elution with a petroleum ether–benzene mixture (70/30) gave 23 mg. of an oil whose infrared was superimposable on that of authentic 1,2,3,4-tetraphenylnaphthalene.

A similar procedure except for the use of temperatures between 275° and 325° was used for mixtures of tetracyclone and other *o*-halobenzoates such as cesium *o*-bromobenzoate, sodium *o*-chlorobenzoate, and potassium *o*-iodobenzoate.

Cesium 2,4-Dichlorobenzoate and Tetracyclone.—Tetracyclone (11.52 g.) and cesium 2,4-dichlorobenzoate (1.62 g.) were mixed and heated in a nitrogen atmosphere between 324–331° for 10 min. Column chromatography of the products gave a fore fraction weighing 0.250 g. and whose infrared in Nujol above 9.0 μ in microns was 9.15 (m), 9.30 (s), 9.96 (m), 10.12 (s), 10.70 (s), 10.90 (m), 11.13 (m), 11.30 (m), 12.0 (s), 12.53 (m), 12.95 (m), 13.42 (s), 14.30 (s), 14.80 (m). The mass spectrum of the oil had the following peaks: 358 (6.1), 398 (7), 468 (35.1), 470 (17.0).

Cesium 2,4-Dichlorobenzoate.—Cesium 2,4-dichlorobenzoate (6.46 g.) was heated in a nitrogen atmosphere between 270° and 297° for 25 min. The acetone–soluble portion of the reaction products was chromatographed to afford 0.245 g. of *m*-chlorophenyl-2,4-dichlorobenzoate, 0.480 g. of mixed dichloroxanthones, and 1.00 g. of material with infrared bands of a ketone and an ester. The respective yields of ester and xanthones were 8.1 and 18%.

Cesium 2,4-Dichlorobenzoate.—Cesium 2,4-dichlorobenzoate (12.93 g.) was heated in a bomb under 100-p.s.i. nitrogen to 325° for 15 min. The maximum pressure was 275 p.s.i.; the final pressure prior to opening of the bomb was 130 p.s.i. Chloroform-soluble material weighed 3.56 g. Chromatography on acid-washed alumina gave dichloroxanthone in 25.6% yield. The 2,6–3,6 isomer ratio was approximately 1. The xanthone accounted for 57.8% of total recovered material. Another 28.9% was ketonic material that came off the column with polar solvents, *e.g.*, ether and methanol.

Silver 2,4-Dichlorobenzoate.—Silver 2,4-dichlorobenzoate (1.649 g.) was heated in a nitrogen atmosphere to 220°, at which point a vigorous evolution of gas took place along with a temperature rise to 240°. After 5 min. the temperature fell to 220° and the reaction flask was removed from the heating bath. Ether washing of the reaction products gave 0.251 g. of material whose infrared was similar to that of a mixture of *m*-chlorophenyl-2,4-dichlorobenzoate and *p*-chlorophenyl-2,4-dichlorobenzoate. Column chromatography did not separate the isomers.

***p*-(*m*)-Chlorophenyl-2,4-Dichlorobenzoate.**—2,4-Dichlorobenzoic acid was converted to the acid chloride with oxalyl chloride, whereupon the latter reacted with an etheral solution of *p*-chlorophenol. After extraction with 5% sodium hydroxide solution, the ether was stripped to a residue which was crystallized twice from methanol, m.p. 225.0–225.5°.

Anal. Calcd. for $C_{13}H_3Cl_3O_2$: C, 51.77; H, 2.34; O, 10.62. Found: C, 52.28; H, 2.73; O, 10.60.

The *m*-chlorophenyl ester was prepared in a similar manner. Its melting point was 99–100°.

Anal. Found: C, 52.08; H, 2.67; O, 10.38.

Potassium 2-(2,4-Dichlorobenzoyloxy)-5-Chlorobenzoate.—2,4-Dichlorobenzoyl chloride (1.91 g.) was added slowly to a cooled solution of 5-chlorosalicylic acid (1.73 g.) in pyridine (15 ml.). After complete addition, the milky mixture was poured into water (150 ml.). The solid was taken up in ether, and the ether solution was washed with 1.2 *N* hydrochloric acid. The ether extract was crystallized from chloroform to melt at 185.5–186.5°. The infrared spectrum had the following bands in Nujol beyond 5.5 μ: 5.70 (s), 5.82 (s), 6.28 (s), 6.4 (m), 6.7 (s), 6.8 (s), 6.92 (s), 7.02 (m), 7.25 (s), 7.65 (s), 7.80 (m), 7.85 (m), 8.05 (s), 8.20 (s), 8.65 (m), 8.95 (s), 9.12 (s), 9.60 (s), 11.1 (m), 11.25 (m), 11.37 (s), 11.93 (s), 12.23 (m), 12.80 (s), 13.12 (s), 14.09 (s), 14.50 (m), and 14.80 μ (s).

Anal. Calcd. for $C_{14}H_7Cl_3O_4$: C, 48.66; H, 2.04; O, 18.52. Found: C, 48.68; H, 2.50; O, 18.21.

2-(2,4-Dichlorobenzyloxy)-5-chlorobenzoic acid, (1.0 g.), was dissolved in 25 ml. of methanol and 25 ml. of ethyl ether. To this solution was added 300 mg. of potassium *t*-butoxide in 20 ml. of methanol. The mixture was stripped at 60° (14 mm.). Ether was added to the residue and filtration gave a white solid whose infrared (Nujol) in microns beyond 5.5 μ was: 5.75 (s), 6.30 (s), 6.85 (s), 7.10 (s), 7.25 (s), 7.65 (m), 7.70 (s), 7.82 (s), 8.05 (s), 8.35 (s), 8.70 (s), 8.95 (s), 9.05 (s), 9.55 (m), 10.10 (m), 11.22 (s), 11.50 (s), 11.60 (m), 11.85 (m), 12.10 (s), 12.60 (s), 13.05 (m), 13.12 (m), 13.80 (s), 14.25 (w), 14.65 (m).

A portion of the salt was added to acidic water. The resulting precipitate was collected and dried. Its infrared was the same as the starting acid.

The potassium salt (0.094 g.) was heated in a nitrogen atmosphere to 310°. At 285° the salt melted with gas evolution. After 5 min. at 310°, the gas evolution subsided and the reaction pot was removed from heat.

Ether washing of the reaction mass dissolved a whitish oil (0.032 g.) whose infrared was identical with that of *p*-chlorophenyl 2,4-dichlorobenzoate. The ether-insoluble residue was dissolved in dilute acid. Extraction with ether followed. The ether solubles (0.030 g.) had the infrared of a mixture of *p*-chlorophenol and 2,4-dichlorobenzoic acid.

5-Chloroaspirin.—5-Chloroaspirin (2.15 g.) was heated to 275° for 20 min. When acetic acid evolution stopped, the temperature was raised to 328° and held at that point for 30 min. The mass was cooled. An infrared of the products in the reaction pot displayed only ester-type carbonyl. The pot was reheated to 362° for 10 min. Another infrared of this reaction mass showed ester and ketonic carbonyl bonds. Column chromatography separated the ketone from the esters. The yield of 2,7-dichloroxanthone was 20%. Its melting point after methanol crystallization was 224–225°; lit.[21] 226°. The infrared (Nujol) of 2.7-dichloroxanthone in microns beyond 5.5 μ was 6.0 (s), 6.23 (s), 6.85 (s), 7.25 (m), 7.60 (m), 7.75 (s), 7.90 (w), 8.25 (m), 8.55 (m), 8.60 (m), 8.80 (s), 9.20 (m), 10.15 (m), 11.0 (s), 11.25 (w), 12.08 (s), 12.20 (s), 12.72 (m), 13.25 (s), 14.42 (s), 14.60 (s).

Anal. Calcd. for $C_{13}H_6Cl_2O_2$: C, 58.89; H, 2.28; O, 26.75. Found: C, 58.76; H, 2.58; O, 26.90.

3,4-Benzocoumarin.—The method of Wittig and Pieper[22] was used to prepare 3,4-benzocoumarin from fluorenone. 3,4-Benzocoumarin (0.400 g.) was heated in a nitrogen atmosphere to 340–345° for 20 min. The ester (0.390 g.) was recovered unchanged, according to infrared analysis.

***o*-Bromobenzoate–*o*-Bromobenzoic Acid.**—*o*-Bromobenzoic acid (13.936 g.) and potassium *o*-bromobenzoate (2.38 g.) were mixed and heated in a nitrogen atmosphere. The maximum temperature was 315° and the heating time above 300° was 16 min. Chromatography of the nonacidic material on acid-washed alumina gave a fraction of 1.276 g. of phenyl *o*-bromobenzoate. The yield based on *o*-bromobenzoate was 46%.

***o*-(*o*-Bromobenzoyloxy)benzoic Acid.**—Salicylic acid was dissolved in pyridine. To this solution was added *o*-bromobenzoyl chloride dropwise with cooling. After complete addition the mixture was poured into water. A white precipitate was collected, dried, and crystallized three times from benzene to melt at 155–156°.

Anal. Calcd. for $C_{14}H_9BrO_4$: C, 52.36; H, 2.38; O, 19.93. Found: C, 52.61; H, 2.51; O, 19.59.

Infrared (Nujol) of acid in microns above 5.0 μ is as follows: 5.70 (s), 5.85 (s), 5.93 (s), 6.23 (s), 6.30 (s), 6.70 (m), 6.82 (s), 6.95 (m), 7.09 (m), 7.25 (m), 7.60 (s), 7.75 (s), 7.85 (s), 10.85 (s), 11.15 (m), 11.40 (w), 11.68 (w), 11.80 (m), 12.42 (m), 12.65 (m), 12.75 (w), 13.23 (s), 13.55 (s), 14.00 (s), 14.60 (s).

o-(*o*-Bromobenzoyloxy)benzoic acid (1.617 g.) was heated in a nitrogen atmosphere to 335°. The time above 300° was 9 min. Temperatures were taken in the reaction mass. The reaction products were treated with ether and chloroform. The ether-soluble material weighed 1.216 g.; the chloroform-soluble material weighed 0.117 g. These two fractions were combined for a chromatography on acid-washed alumina. Phenyl *o*-bromobenzoate (0.071) g. was recovered from a petroleum ether (30–60°)–benzene mixture (85/15). The total material taken off the column was 0.4948 g. The yield of phenyl *o*-bromobenzoate was 5.1%.

Potassium *o*-Iodobenzoate.—Potassium *o*-iodobenzoate (11.54 g.) was heated in a nitrogen atmosphere between 320° and 330° for 15 min. Upon cooling, the reaction mass was treated with ether. The ether-soluble material weighed 1.81 g. and was chromatographed on acid-washed alumina. The following materials were isolated and identified by infrared spectra and v.p.c.: phenyl *o*-iodobenzoate (0.044 g.), xanthone (0.100 g.), and benzocoumarin (0.704 g.). The yields of xanthone and benzocoumarin based on starting material are 2.5% and 18%, respectively. Two unknown materials were also isolated: a hydrocarbon (0.102 g.) with infrared absorptions at 6.4, 6.95, 8.0, 9.2, 9.75, 9.95, 10.15, and 13.5 μ; an ester (0.065 g.) with infrared absorptions at 5.8, 6.2, 6.85, 7.65, 8.35, 8.6, 9.1 and 10.8 μ.

Potassium *o*-(*o*-Iodobenzoyloxy)benzoate.—*o*-Iodobenzoic acid was converted to its acid chloride by means of oxalyl chloride. The acid chloride was poured into a chilled solution of salicylic acid in pyridine. After addition, the pyridine solution was poured into excess acidic water and the precipitate so formed was collected. Two crystallizations from benzene gave white crystals melting at 147–148°. Its infrared spectrum (Nujol) in microns beyond 5.0 μ is as follows: 5.70 (s), 5.85 (s), 6.23 (s), 6.30 (m), 6.40 (m), 6.70 (m), 6.85 (s), 7.10 (m), 7.25 (m), 7.65 (s), 7.80 (s), 8.05 (s), 8.30 (s), 8.60 (s), 8.82 (s), 9.20 (s), 9.60 (m), 9.85 (s), 10.85 (m), 11.15 (m), 11.80 (m), 12.45 (m), 12.65 (m), 12.80 (m), 13.30 (s), 13.70 (s), 14.10 (s), 14.68 (s).

Anal. Calcd. for $C_{14}H_9IO_4$: C, 45.69; H, 2.47; O, 17.38. Found: C, 45.86; H, 2.17; O, 17.38.

The *o*-(*o*-iodobenzoyloxy)benzoic acid (0.368 g.) was dissolved in ether and treated with 0.100 g. of potassium *t*-butoxide in 10 ml. of *t*-butyl alcohol. The mixture was stripped of solvent at 60° (90 mm.). The residue weighed 0.200 g. and had the following infrared spectrum (Nujol) in microns above 5.0 μ: 5.70 (s), 6.23 (s), 6.40 (s), 6.85 (s), 7.0 (m), 7.30 (s), 7.75 (m), 7.90 (m), 8.15 (s), 8.40 (s), 8.60 (w), 8.70 (m), 8.88 (s), 9.20 (s), 9.25 (m), 9.60 (s), 9.85 (s), 10.50 (w), 10.60 (w), 11.25 (m), 11.50 (w), 11.65 (m), 11.90 (w), 12.25 (m), 12.40 (m), 12.70 (m), 13.50 (s), 13.65 (s), 14.20 (s), 14.50 (w), 14.80 (m).

The potassium *o*-(*o*-iodobenzoyloxy)benzoate (0.200 g.) was heated under a nitrogen atmosphere at 260° for 10 min. The reaction mass, upon cooling, was treated with chloroform. A v.p.c. of the chloroform-soluble material showed the presence of phenyl *o*-iodobenzoate, 3,4-benzocoumarin, phenyl benzoate, and xanthone. The column for this analysis was composed of chromosorb with 5% SE 30 silicone oil and was heated at 260°.

Silver *o*-Iodobenzoate.—Silver *o*-iodobenzoate (2.456 g.), prepared by the reaction of silver nitrate and potassium *o*-iodobenzoate, was heated in a nitrogen atmosphere to 80°, at which point a rapid exothermic reaction took place. The temperature rose to 155°. Diphenic anhydride (0.050 g.) was isolated from the top of the reaction vessel. The ether-soluble reaction products (0.530 g.) were chromatographed on acid-washed alumina. The various chromatographic cuts were examined by v.p.c. on 5% SE 30 on Chromosorb (temp., 266°). The following were identified: phenyl benzoate, phenyl *o*-iodobenzoate, xanthone, and 3,4-benzocoumarin. The yield of 3,4-benzocoumarin was 10%; that of xanthone was 5%; that of phenyl *o*-iodobenzoate was 5%; that of phenyl benzoate was 10%.

Silver *o*-iodobenzoate (4.72 g.) was heated under vacuum to 120°. Gas evolution was vigorous but not violent. Acetone washing of the reaction products afforded 0.161 g. of material with an ester infrared spectrum. Ether washing gave only 0.008 g. Chloroform washing gave 1.631 g. of tacky material. The latter residue was redissolved in 10 ml. of chloroform and poured into petroleum ether (30–60°). A precipitate formed which was filtered and dried. Its melting range was 135–143°. Its molecular weight by ebullioscopic determination with chloroform was 3150. The infrared of this oligomer in Nujol beyond 5.0 μ in microns was as follows: 5.69 (s), 6.21 (m), 6.42 (w), 6.73 (w), 6.85 (s), 7.75 (m), 7.79 (s), 8.01 (s), 8.30 (s), 8.62 (m), 8.90 (m),

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(21) H. E. Faith, M. E. Bahler, and H. J. Florestano, *J. Am. Chem. Soc.*, **77**, 543 (1955).

(22) G. Wittig and G. Pieper, *Ber.*, **73**, 295 (1940).

9.01 (w), 9.32 (m), 9.51 (s), 9.77 (m), 11.17 (w), 11.75 (w), 12.80 (w), 13.42 (s), 14.55 (w).

Anal. Found: C, 55.01; H, 3.09; O, 21.78; Ag, 8.85; I, 9.74.

A portion of the oligmer (0.191 g.) was hydrolyzed with base to salicylic acid (0.111 g.).

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Fate of the Carbinol Carbon in the Conversion of Tetrahydrofurfuryl Alcohol to Dihydropyran

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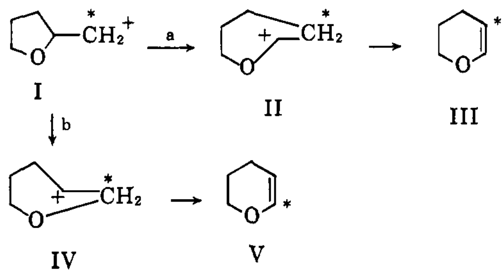
Tetrahydrofurfuryl alcohol with carbon-14 in the exocyclic carbon atom was prepared by carbonating furyllithium with radioactive carbon dioxide and reducing the resulting furoic(^{14}COOH) acid. Lithium aluminum hydride converted the acid to furfuryl alcohol. Hydrogen over Raney nickel then saturated the ring to give the labeled tetrahydrofurfuryl alcohol. Passing the labeled alcohol over hot alumina produced radioactive dihydropyran. Ozonization cleaved the dihydropyran to formic acid and 4-hydroxybutanal, while nitric acid oxidation of the dihydropyran gave glutaric acid which with hydrazoic acid was degraded to 1,3-diaminopropane. The results of radioactivity assays on these materials showed that the carbon-14 in dihydropyran was located in the 2- and 6-positions. The relations of this distribution to postulated reaction pathways is discussed.

When tetrahydrofurfuryl alcohol is passed over alumina at 350°, dehydration and ring expansion occur to give dihydropyran.[1,2] Although the reaction has been examined and improved by several groups,[3-5] only little evidence useful in defining a mechanism has been obtained. We wish to report work bearing on this aspect of the tetrahydrofurfuryl alcohol–dihydropyran conversion.

In the first stages of the reaction, alumina may be taken to coordinate with one or both of the oxygen atoms in tetrahydrofurfuryl alcohol. We assumed as a working hypothesis that the hydroxyl oxygen is the one involved and, therefore, that the exocyclic carbon atom becomes electron deficient. This presents two rearrangement possibilities, which are formulated here—in terms of the limiting carbonium ion-form I[6]—as paths a and b. Path a proceeds through a Wagner–Meerwein rearrangement with ring expansion (see II) and loss of proton to give the dihydropyran product III. A close analogy may be found in the alumina dehydration of cyclopentylcarbinol to cyclohexene.[10] An added favorable feature is the possibility of delocalization of the positive charge in II to oxygen.[11] Path b has the ring oxygen migrating to the external methylene group to give IV, which on loss of a proton becomes dihydropyran V. An ethylene oxide ring derived from IV could be involved in the rearrangement just as in the conversion of 2-methoxy-2-methylpropyl *p*-bromobenzenesulfonate to isobutyraldehyde.[12] A basis of choice between paths a and b lay in the fact that the former places the exocyclic carbon atom of tetrahydrofurfuryl alcohol at the dihydropyran 3-position (*cf.* III), while the latter places it at the dihydropyran 2-position (*cf.* V). With this in mind, we proceeded to prepare tetrahydrofurfuryl alcohol with carbon-14 in the exocyclic methylene group, to carry out the dehydration–rearrangement, and to locate the carbon-14 in the derived dihydropyran.



In order to obtain the labeled starting alcohol, furyllithium was carbonated with radioactive carbon dioxide. Lithium aluminum hydride converted the resulting furoic(^{14}COOH) acid (VI) to furfuryl alcohol,

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(1) The formal names for this compound and its derivatives are cumbersome and unfamiliar. Thus, for the parent compound we have our choice of 5,6(or 2,3)-dihydro-4*H*-pyran, 5,6(or 2,3)-dihydro-γ-pyran, or 5,6(or 2,3)-dihydro-1,4-oxin. For convenience, we have based the naming here on Δ^2-dihydropyran and, wherever possible, have dropped the Δ^2. Note that this scheme automatically places the double bond at the 2,3- rather than the 5,6-position.

(2) R. Paul, *Bull. soc. chim.*, [4] **53**, 1489 (1933).

(3) R. L. Sawyer and D. W. Andrus, *Org. Syn.*, **23**, 25 (1943).

(4) L. E. Schniepp and H. H. Geller, *J. Am. Chem. Soc.*, **68**, 1646 (1946).

(5) C. H. Kline and J. Turkevich, *ibid.*, **67**, 498 (1945).

(6) The tetrahydrofurfuryl cation has been suggested before as a key intermediate: *cf.* Paul,[7] who interpreted his reaction in terms of something resembling the cation, Wilson,[8] and Fried.[9]

(7) R. Paul, *Bull. soc. chim.*, [5] **2**, 745 (1935).

(8) G. J. Baumgartner and C. L. Wilson, *J. Am. Chem. Soc.*, **81**, 2440 (1959); H. P. Thomas and C. L. Wilson, *ibid.*, **73**, 4803 (1951).

(9) J. Fried, "Heterocyclic Compounds," Vol. I, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 348.

(10) H. S. Turner and R. J. Warne, *J. Chem. Soc.*, 789 (1953).

(11) Other pertinent analogies involving a carbon shift to the adjacent electron-deficient carbon may be cited. These include diazotization of cyclopentylmethylamine to cyclohexanol [P. A. S. Smith, D. R. Baer, and S. N. Ege, *J. Am. Chem. Soc.*, **76**, 4564 (1954)], of 2-(aminomethyl)-tetrahydrofuran to an "oxidation product" of 5-hydroxypentanal [N. V. Williams, *Chem. Abstr.*, **26**, 3253 (1932); *Bull. acad. sci. USSR, Classe sci. math. nat.*, 1117 (1931)], and of 2-(aminomethyl)-tetrahydropyran to 6-hydroxyhexanal [J. Colonge and P. Corbet, *Bull. soc. chim. France*, 287 (1960); *Compt. rend.*, **247**, 2144 (1958)]. The rearrangement of pinacol to pinacolone over alumina at 320° [W. N. Ipatieff and W. Leontowitsch, *Chem. Zentr. II*, **77**, 87 (1906); *J. Russ. Phys. Chem. Soc.*, **35**, 606 (1903)], the conversion of 4-hydroxy-2,4,6-trimethyl-2,5-cyclohexadienone to trimethylhydroquinone with dilute acid [E. Bamberger and A. Rising, *Ber.*, **33**, 3636 (1900)], and the transformation of 3-ethoxy-2-methyl-2-heptanol to 2,2-dimethylhexaldehyde in hot formic acid [I. Elphimoff-Felkin, *Bull. soc. chim. France*, 497 (1950)] are also related.

(12) S. Winstein, C. R. Lindegren, and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 155 (1953). Other examples of the migration of oxygen to an adjacent electron-deficient carbon atom may be found in the solvolysis of tetrahydrofurfuryl tosylate and bromide to 3-hydroxytetrahydropyran [D. Gagnaire, *Bull. soc. chim. France*, 1813 (1960)] and in the isomerization of tetrahydrofurfuryl acetate to 3-acetoxytetrahydropyran in the presence of zinc chloride [D. Gagnaire and A. Butt, *ibid.*, 309 (1961)].