The mechanism of the action of the promoters has been studied and found to be due partly to the prevention of decay of the enzyme. The greater part of the action of the promoter is not due to this but to a specific stimulating action of the amino compound.

Any possible hydrogen-ion effect has been eliminated by the use of a buffer.

Iowa City, Iowa

[Contribution from the Chemical Laboratory of Johns Hopkins University]

ORTHO-BENZOYL-BENZOIC ACIDS CONTAINING FLUORINE, IODINE AND SULFUR[1]

By Frederick C. Hahn and E. Emmet Reid

Received February 25, 1924 Published July 7, 1924

On account of their ready conversion into anthraquinone derivatives the substituted *o*-benzoyl-benzoic acids have been extensively studied. As the chloro- and bromobenzoyl-*o*-benzoic acids and a number of their methyl derivatives are well known, it seemed of interest to investigate the corresponding fluoro- and iodo-compounds. In addition the methyl ether of thiophenol has been condensed with phthalic anhydride. The *o*-benzoyl-benzoic acids obtained have been condensed to anthraquinone derivatives.

Results

All condensations were made in the usual way using two molecules of aluminum chloride to one each of phthalic anhydride and the substituted hydrocarbon.

Fluoro-benzoyl-*o*-benzoic Acid and Methyl Derivatives.—Fluorobenzene condenses readily to give the 4′-acid.[2] This constitution was assumed on account of analogy with the chloro- and bromo-acids.[3] Fluorine orients a negative group to the *para* position even more strongly than the other halogens, since the nitration of fluorobenzene yields 90% of *p*-nitrofluorobenzene. This constitution was proved by the fact that the acid formed yields *p*-hydroxybenzoyl-*o*-benzoic acid[4] when boiled with a concd. solution of sodium hydroxide. The hydroxy acid proved to be identical with that prepared by Friedländer.

From *p*-fluorotoluene two acids, I and II, are possible. The low melting point of the crude acid and of crystals from the mother liquors even after it is recrystallized, appears to indicate that both are formed; but one predominates and is easily obtained pure. Since it has been shown

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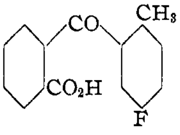
[1] From the Doctor's Dissertation of Frederick C. Hahn, **1923.**

[2] Ger. pat. 75,288; Meister, Lucius and Brüning.

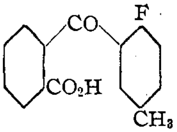
[3] Ullmann, *Ann.*, **380,** 337 (1911).

[4] Friedländer, *Ber.*, **26,** 176 (1893).

by Swarts[5] that methyl has a stronger orienting influence than fluorine, the acid isolated is probably I. Both I and II must condense to the same anthraquinone and, as a matter of fact, the condensation product from the low melting crude acid was practically as pure as that from the purified acid.

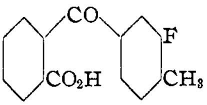


I

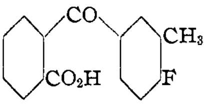


II

With *o*-fluorotoluene there are four possibilities, III, IV, V and VI. One crystallization gave a practically pure acid, indicating that one isomer greatly predominates. When this was condensed to methyl-fluoro-anthraquinone, the methyl group was oxidized and eliminated, and *β*-fluoroanthraquinone was formed. This disposes of formula VI. It is known[6] that when *o*-chlorotoluene reacts with phthalic anhydride and the resulting acid is condensed, the product is 2-methyl-3-chloro-anthraquinone. Analogy with this makes Formula V improbable. From the orienting influence of the groups as shown by Swarts,[4] we may conclude that the acid is *p*-methyl-*m*-fluorobenzoyl-*o*-benzoic acid, III.



III



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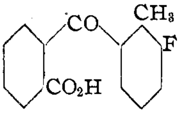

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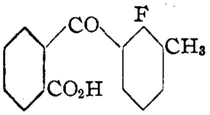
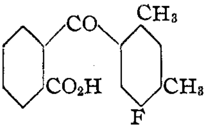
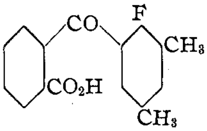


VI

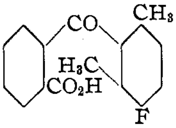
With 4-fluoro-*m*-xylene three isomers, VII, VIII and IX, are possible. The crude acid was a viscous mass which could not be induced to crystallize and was assumed to be a mixture. It condenses partly to form what must be 2,3-dimethyl-4-fluoro-anthraquinone. The acid obtained by extracting this with alkali must be represented by IX, since it cannot be condensed. The acid that does condense must have Formula VII, since substitution would certainly have taken place, *ortho-para* to the two methyl groups rather than *meta* to both of them.



VII



VIII



IX

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[5] Swarts, *Rec. trav. chim.*, **35,** 131 (1915).

[6] Heller and Schülke, *Ber.*, **41,** 3627 (1908). Ullmann and Dasgupta, *Ber.*, **47,** 553 (1914).

Experimental Part

The aromatic fluorine derivatives used in the following preparations were made according to the method of Holleman.[7] 4-Fluoro-*m*-xylene, which he did not prepare, was obtained similarly with a yield as good as those of the other fluorides.

The acids were isolated from the excess of reactants in the usual manner, by steam distillation; the residue was dissolved in alkali, the solution filtered and the materials were precipitated by the addition of dil. hydrochloric acid. They are all white. When precipitated rapidly from solutions of their salts they separated as a viscous mass; *o*-benzoyl-benzoic acid behaves similarly.

Details of several preparations are given in tabular form.

TABLE I

PREPARATION OF FLUORO ACIDS

Acid from	Phthalic anhydride G.	Aromatic fluoride G.	Aluminum chloride G.	Yield G.	% Yield on basis of phthal. anhyd.
p-Fluorobenzene	28	38	56	41.5	90
p-Fluorotoluene	27	40	54	45	96
o-Fluorotoluene	54	83	108	90	96
4-Fluoro-*m*-xylene	38	63	76	..	..

TABLE II

PROPERTIES AND ANALYSES OF FLUORO ACIDS

Benzoyl-benzoic acids	M. p. °C.	Mol. wt. (titration) Calc.	Mol. wt. (titration) Found	% Fluorine Calc.	% Fluorine Found
p-Fluoro	137–137.5	244	246	7.78	7.96, 7.71, 7.69
2-Methyl-4-fluoro-	150	258	256.8	7.36	7.42, 7.18, 7.14, 7.20
4-Methyl-3-fluoro-	153.5–154	258	257	7.36	7.58

The acids listed above are appreciably soluble in benzene, in alcohol and in glacial acetic acid, but practically insoluble in water. *p*-Fluoro-benzoyl-*o*-benzoic acid crystallizes from benzene with one molecule of benzene in combination.

The conversion of the acids into the anthraquinones occurs when they are dissolved in concd. or fuming sulfuric acid and heated between 100° and 150°. The resulting solutions are cooled and poured into ice water. The

TABLE III

FLUORO-ANTHRAQUINONES

	Preparation							Properties and analyses		
Anthraquinone	Wt. of acid G.	Wt. of H_2SO_4 G.	Concn.	Temp. °C.	Time Hours	Yield G.	Yield %	M. p. °C.	% Fluorine Calc.	% Fluorine Found
β-Fluoro-	2	20	95%	150–160	1/2	..	Quant.	203–4	8.40	8.10, 8.28, 8.64
1-Methyl-4-fluoro-	2	20	23% SO_3	100	1/2	..	Quant.	155-6	7.91	7.84, 7.80, ...
2-Methyl-3-fluoro-	5	50	23% SO_3	100	1	4.5	96	172	7.91	7.70 ....
1,3-Dimethyl-4-fluoro-	50	250	23% SO_3	100	1	34	73	178	7.48	7.11, 7.01 ....

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[7] Holleman, *Rec. trav. chim.*, **23**, 233, 238 (1904).

precipitated anthraquinone, purified by extraction with sodium hydroxide solution, is finally recrystallized.

All of these substituted anthraquinones have the characteristic properties of analogous anthraquinone compounds; all are pale yellow.

Hydrolysis of Fluoro Acid (I).—A mixture of 1 g. of *p*-fluoro-benzoyl-*o*-benzoic acid and 25 cc. of 50% sodium hydroxide solution was refluxed for 4 to 5 hours. The mixture was diluted with water, acidified, evaporated to dryness and the residue extracted with sodium carbonate solution. After filtering the solution, the acid was precipitated by acidifying the filtrate. Recrystallized from hot water it melted at 213°. *p*-Hydroxy-benzoyl-*o*-benzoic acid was prepared according to the method of Orndorff and Murray;[8] it melted at 213°, which showed that it was identical with our product.

The diacetyl derivatives of both products were prepared according to the method of Orndorff and Kelley[9] and found to be identical.

***p*-Fluoro-benzyl-*o*-benzoic Acid.**—The fluoro-benzoyl acid was reduced exactly according to the method of Scholl, Potschiwauscheg and Lenko[10] for ethylbenzyl-*o*-benzoic acid. It was recrystallized from dil. alcohol and finally from benzene; m. p., 148–149°.

Analysis. Calc. for $C_{14}H_{11}O_2F$: F, 8.26. Found: 7.78.

***o*-Carboxy-fluorobenzoyl-*o*-Benzoic Acid.**—To a solution of 2 g. of *o*-fluorotoluyl-*o*-benzoic acid in 10 cc. of 2 *N* sodium hydroxide solution, warmed on a water-bath, 0.2 *N* potassium permanganate solution was added until the pink color persisted. The excess of permanganate was decomposed with alcohol, the mixture filtered, and the acid precipitated from the filtrate; yield, 1.8 g. It may be crystallized from dil. alcohol or acetic acid. Even after several crystallizations it gave no sharp melting product; it sintered at 175° and melted at 183–184°. The molecular weight by titration was 296; that calculated was 288.

Analysis. Calc. for $C_{15}H_9O_5F$: F, 6.59. Found: 6.72.

2-Fluoro-3-carboxy-anthraquinone.—A mixture of 2 g. of 2-fluoro-3-methyl-anthraquinone, 12 cc. of water and 4 g. of 70% nitric acid was heated in a sealed tube at 200–210° for 5 hours. After the tube had cooled, yellow crystals of the acid separated; these were collected on a filter and crystallized from dil. acetic acid; m. p., 183–185°. When this acid is heated, carbon dioxide is evolved abundantly and β-fluoro-anthraquinone is formed. The identity of this product was established by the method of mixed melting points.

Analysis. Calc. for $C_{15}H_7O_4F$: F, 7.03. Found: 6.73.

1-Fluoro-4-carboxy-anthraquinone.—A mixture of 1 g. of 1-fluoro-4-methylanthraquinone, 4 cc. of water and 2 g. of 66% nitric acid was heated in a sealed tube at 195–200° for 5 hours. The product was isolated by the method used for the acid just described. No distinct melting point could be obtained; the substance shrinks gradually between 200° and 250°, after which it melts completely and commences to decompose with the evolution of carbon dioxide. The yellow sublimate of needles which formed was treated with alkali, in which it was insoluble, and then recrystallized from glacial acetic acid; m. p., 128–129°. It is probably α-fluoro-anthraquinone.

Analysis. Calc. for $C_{15}H_7O_4F$: F, 7.03. Found: 6.69.

2,6-Dimethyl-3-fluorobenzoyl-*o*-benzoic Acid. (IX).—The crude acid from the

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[8] Orndorff and Murray, THIS JOURNAL, **39**, 680 (1917).

[9] Orndorff and Kelley, *ibid.*, **44**, 1522 (1922).

[10] Scholl, Potschiwauscheg and Lenko, *Monatsh.*, **32**, 692 (1911).

condensation of fluoro-xylene with phthalic anhydride was a viscous mass that could not be crystallized. This acid cannot be condensed to an anthraquinone as both of the *ortho* positions to the carbonyl group are occupied by methyl groups. When the crude mixture of dimethyl-fluorobenzoyl-benzoic acids is treated with concd. sulfuric acid this one is not affected and may be extracted from the crude dimethyl-fluoro-anthraquinone by means of sodium hydroxide solution. It is quite soluble in benzene, acetic acid and alcohol, but very slightly soluble in petroleum ether. From a mixture of acetic acid and water it crystallizes as yellow needles melting at 126°. Its molecular weight, determined by titration, was 275; that calculated was 272.

Analyses. Calc. for $C_{16}H_{13}O_3F$: F, 6.98. Found: 6.74, 6.54.

p-Iodobenzoyl-o-benzoic Acid.—A mixture of 210 g. of freshly distilled iodobenzene, 148 g. of powdered phthalic anhydride and 400 cc. of carbon disulfide, cooled in an ice bath and agitated, was treated with 296 g. of powdered aluminum chloride added in portions during a period of half an hour. After all the aluminum chloride had been added the mixture was agitated for four hours at room temperature, and then for ten hours at the refluxing temperature of the mixture. The carbon disulfide was then distilled and the viscous residue heated for three hours at 80–85°. The reaction mixture was then worked up in the usual manner. Large quantities of iodine came over during the steam distillation. The residue was extracted with alkali and the crude acid isolated in the usual way; yield, 179 g. The crude acid was recrystallized from various solvents, but melting points varied from 86° to 96° and were sometimes higher. Since such large quantities of iodine were liberated it was evident that the product could not contain any considerable proportion of iodobenzoyl-benzoic acid, and that this acid could not be isolated from the mixture by means of crystallization. The p-iodobenzoyl-o-benzoic acid was isolated as described below and after recrystallization from acetic acid, melted at 200°. The molecular weight was found by titration to be 345.5; that calculated was 352.

p-Iodochloride-benzoyl-o-benzoic Acid.—The crude acid just described was dissolved in 4 parts of chloroform, the solution filtered from a small amount of insoluble material, and dry chlorine was passed in until no more was absorbed. The yellow granular precipitate was collected on a filter quickly, washed with dry chloroform and dried in a vacuum desiccator. It retains a very slight odor of chlorine and, when heated, melts and gives off chlorine readily without the explosion which characterizes this type of compound. For analysis a weighed amount of this acid was treated with chloroform, water and potassium iodide, and the liberated iodine titrated with standard thiosulfate solution. Analyses for chlorine were low for the acid as isolated by the method described above. This acid was treated with an excess of thiosulfate solution, and the resulting iodobenzoyl-benzoic acid purified by recrystallization and then reconverted into the iodochloride acid.

Analysis. Calc. for $C_{14}H_9O_3ICl_2$: Cl, 16.77. Found: 16.70.

The iodochloride acid is converted into iodobenzoyl-benzoic acid by treatment with chloroform, water and sodium thiosulfate. The chloroform layer, when evaporated, leaves a beautiful, flaky, crystalline residue.

β-Iodo-anthraquinone.—Condensation of the p-iodobenzoyl-o-benzoic acid was effected in the usual manner with sulfuric acid at 150–160° for one hour. The crude product melted at 174–175°. Recrystallized from acetic acid, it melted sharply at 175°, showing it to be β-iodo-anthraquinone. The fact that the crude product had such a good melting point shows that the iodo acid must have been the *para* acid, since the *meta* acid would have given a mixture of α- and β- iodo-anthraquinones.

An investigation of the by-products formed in this condensation of iodo-benzene and phthalic anhydride showed that o-benzoylbenzoic acid was the main product. This was determined by its conversion into anthraquinone and by the method of mixed melting points.

_p_-Iodosobenzoyl-_o_-benzoic Acid.—A solution of 2 g. of *p*-iodochloride-benzoyl-*o*-benzoic acid in 20 cc. of 2 *N* sodium hydroxide solution was allowed to stand for one hour at room temperature. It was then cooled and acidified very slightly with dil. hydrochloric acid; this precipitated the iodoso acid in crystalline form. It melts at 179–180°, and does not give up any appreciable amount of oxygen when heated to 250°, but when heated considerably above this temperature it gives up its iodoso oxygen with violence; mol. wt. (by titration), 358.1; calcd., 368.

Methyl Ether of _p_-Mercapto-benzoyl-_o_-benzoic Acid.—A mixture of 25 g. of methylphenyl sulfide and 15 g. of phthalic anhydride was treated with 30 g. of aluminum chloride and heated for four hours at 80°. The reaction product was decomposed with water and treated in the usual manner. The yield of the crude acid was 22 g. It crystallizes from benzene in fine white needles melting at 154°.

Analyses. Calc. for $C_{15}H_{12}O_3S$: S, 11.76. Found: 11.65, 11.57.

_p_-Methylsulfonyl-benzoyl-_o_-benzoic Acid.—To a solution of 2 g. of this mercapto acid in 25 cc. of glacial acetic acid, 1.2 g. of chromic anhydride was added. The mixture was refluxed until the liquid was distinctly green and then poured into 150 cc. of water. After several minutes, white, flaky crystals of the sulfone separated in very pure form. The product, purified by crystallization from glacial acetic acid, melts at 221°.

Analysis. Calc. for $C_{15}H_{12}O_5S$: S, 10.54. Found: 10.63, 10.49.

β-Methylsulfone of Anthraquinone.—One part of *p*-methyl-sulfonyl-*o*-benzoyl-benzoic acid was dissolved in 20 parts of concd. sulfuric acid, and the mixture heated at 160° for one hour, during which the solution became a deep red. It was then poured onto ice and treated in the usual manner. The crude product melts at 228–230° but, after recrystallization from benzene, it melts sharply at 230°; this agrees exactly with the melting point of the product prepared by Gattermann.[11] This shows that the constitutions of the two compounds described above are as stated.

Esters of Substituted *o*-Benzoyl-Benzoic Acids

Esters of some of the acids described above and of some known acids were prepared by treating these acids with an excess of alcohol and a drop of sulfuric acid, and refluxing the mixture for several hours. The propyl and butyl esters of *p*-fluorobenzoyl-benzoic acid are both oils that did not crystallize. They distil in a vacuum with practically no decomposition, the propyl at 200° and the butyl ester at 225° under 8 mm. pressure. The esters were saponified by standard alkali. Their properties are given in Table IV.

TABLE IV

ESTERS OF SUBSTITUTED *o*-BENZOYL-BENZOIC ACIDS

Alkyl	Acid	M. p. °C.	Neutral equivalent	
			Calcd.	Found
Methyl	*p*-Fluorobenzoyl-*o*-benzoic	93.5	258	257.3
Ethyl		80.5	272	267
Propyl		Oil		
Butyl		Oil		

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[11] Gattermann, *Ann.*, **393**, 150 (1912).

TABLE IV (*Concluded*)

Alkyl	Acid	M. p. °C.	Neutral equivalent Calcd.	Found
Methyl	*p*-Chlorobenzoyl-*o*-benzoic	110	275	273
Ethyl		88	289	286
Propyl		45	303	300
Butyl		Oil		
Methyl	*p*-Bromobenzoyl-*o*-benzoic	104	319	317
Ethyl		83.5	333	330
Propyl		51	347	336
Butyl		Oil		
Methyl	*p*-Iodobenzoyl-*o*-benzoic	104–104.5	366	359
Ethyl		81.5–82	380	376
Propyl		52	394	389
Butyl		Oil		
Methyl	*m*-Nitrobenzoyl-*o*-benzoic	100	285	285
Ethyl		84	299	295
Methyl	2-Methyl-4-fluorobenzoyl-*o*-benzoic	79.5–80	272	273
Ethyl		Oil	286	288
Methyl	4-Methyl-3-fluorobenzoyl-*o*-benzoic	108	272	272
Ethyl		74	286	285

Estimation of Fluorine

Methods of estimating fluorine in organic compounds have been proposed by Beckmann,[12] Meyer and Hub,[13] and Paterno.[14] A history of fluorine methods in general with many references is given by Wagner and Ross.[15] It has been shown by Pringham,[16] Parr and Lemp[17] and Broderson[18] that sulfur, chlorine, bromine and iodine may be satisfactorily determined by fusion with sodium peroxide. We decided to try this method for our fluorine compounds. The fluorine was precipitated and weighed as calcium fluoride as proposed by Berzelius[19] and Rose.[20] Later we found that this method had been tried in the Chemical Warfare Service Laboratory at Edgewood Arsenal.[21] On account of the many difficulties introduced by the solubility of calcium fluoride, on the one hand, and contamination of the precipitate with silica and calcium carbonate on the other, we were unable to get satisfactory results with the method as obtained from the Edgewood Arsenal, but by adopting more precise condi-

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[12] Beckmann, *Rec. trav. chim.*, **23,** 239 (1905).

[13] Meyer and Hub, *Monatsh.*, **31,** 937 (1910).

[14] Paterno, *Gazz. chim. ital.*, **49,** 371 (1919); *Analyst,* **43,** 147 (1917).

[15] Wagner and Ross, *J. Ind. Eng. Chem.*, **9,** 1117 (1917).

[16] Pringham, *Am. Chem. J.*, **31,** 386 (1904).

[17] Parr and Lemp, THIS JOURNAL, **30,** 764 (1908).

[18] Broderson, *ibid.*, **39,** 2069 (1917).

[19] Berzelius, *Pogg. Ann.*, **1,** 69 (1824); *Schweigg. J.*, **16,** 426 (1816).

[20] Rose, *Ann.*, **72,** 343 (1849).

[21] The method used there was kindly furnished us by Mr. H. C. Knight in charge of the Analytical Department.

tions for the precipitation and washing of calcium fluoride, as given below, concordant analyses were obtained.

Method of Analysis.—About 0.4 g. of the test substance is mixed intimately with 12–14 g. of sodium peroxide and 0.4 g. of starch in a Parr bomb. Without the starch there was incomplete decomposition. The mixture is ignited by holding the bomb in a hot flame and the fusion point is usually noted by the bomb suddenly turning red from the bottom to about one-fourth its height. It is immediately cooled in running water. The fused mass should be gray with little or no unburned carbon. After the contents of the bomb are dissolved in water, the solution is boiled until all of the sodium peroxide is decomposed, diluted to 400 cc. and filtered. To the filtrate 10% hydrochloric acid is added drop by drop until it is just acid to methyl red and then 2 cc. of 2 *N* sodium carbonate solution is added at once. The mixture is evaporated over a free flame to a volume of 125 cc. and the silicic acid collected on a filter and washed. The filtrate is evaporated in a Pyrex beaker to about 100 cc. and 10 cc. of 20% calcium chloride solution is added drop by drop to the hot solution. The mixture is heated almost to boiling for a few minutes, cooled and filtered through an ashless filter. It is unnecessary to wash the precipitate thoroughly. The filter and its contents are dried at 110° and the contents transferred as completely as possible to a 100cc. platinum dish.[22] The filter is then burned on a platinum spiral, the residue transferred to the same dish, 10 cc. of water added to the combined residues, and a 10% solution of acetic acid added until effervescence caused by calcium carbonate ceases, which should not require over 10 cc. The mixture is evaporated on a hot-plate to dryness until the odor of acetic acid has passed, and then heated for a half hour longer to change the calcium fluoride to a granular form. The residue is treated with 10 cc. of water and stirred until the calcium acetate is dissolved. The calcium fluoride is washed with 10 cc. of water by decantation, collected on an ashless filter, and washed with a minimum quantity of water until the filtrate gives no turbidity upon the addition of a drop of sodium fluoride solution. The filter and contents are ignited to constant weight in a platinum crucible in the hot flame of an ordinary burner. The calcium fluoride may be confirmed by conversion to the sulfate but, in general, this is not necessary.

Summary

It has been found that the condensation of various aromatic fluorides with phthalic anhydride by means of aluminum chloride proceeds with the formation of correspondingly substituted benzoyl-*o*-benzoic acids in a normal manner. The condensation between iodobenzene and phthalic

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[22] It was found that just as good results were obtained when a small Pyrex beaker was used instead of a platinum dish, by not adding more acetic acid than necessary to dissolve the calcium carbonate.

anhydride gives a very small yield of the anticipated iodobenzoyl-*o*-benzoic acid, but large quantities of benzoyl-*o*-benzoic acid and iodine. These acids are easily converted to the corresponding anthraquinones by being heated with sulfuric acid. It has likewise been shown that the methyl thio ether of mercapto-benzoyl-*o*-benzoic acid may be synthesized by this method. A detailed procedure for the analysis of organic compounds for fluorine has been worked out.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

A STUDY OF THE CHEMICAL BEHAVIOR OF ALPHA- AND BETA-HYDROFORMAMINE CYANIDES

BY H. W. RINEHART AND TREAT B. JOHNSON[1]

RECEIVED MARCH 14, 1924 PUBLISHED JULY 7, 1924

The substances, α- and β-hydroformamine cyanides, which melt at 129° and 86°, respectively, are isomeric compounds that result by the interaction of formaldehyde, ammonium chloride and potassium cyanide. These substances, which have hitherto been registered in chemical literature by the name *methylene aminoacetonitrile*, possess the empirical formula $C_9H_{12}N_6$, but are of unknown constitution.[2] In order to acquire a knowledge of the molecular structure of these two isomeric compounds, we have begun a comparative investigation of their chemical behavior. This research has already opened up several new chemical problems of both theoretical and practical interest. Furthermore, in a preliminary pharmacological research these substances have been found to possess interesting physiological properties which have also led to a renewed interest in the constitution of these compounds. In this paper, therefore, new data will be presented which reveal characteristic differences in chemical behavior between these isomers, and from which we are able to deduce fundamental conclusions with respect to their chemical constitution.

α-Hydroformamine cyanide behaves like a saturated compound and in no reaction thus far applied has definite evidence been obtained that it contains the unsaturated ethylene linkages which are characteristic of Schiff bases. The results obtained by Delepine[3] with hydrocyanic acid and, also, the fact that no reduction has been observed to take place with production of methylamino groups are experimental results quite in accord with the behavior of a saturated compound.

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[1] Constructed from a dissertation presented by H. W. Rinehart in 1923 to the Faculty of the Graduate School of Yale University in Candidacy for the degree of Doctor of Philosophy.

[2] Johnson and Rinehart, THIS JOURNAL, **46**, 768 (1924).

[3] Delepine, *Bull. soc. chim.*, [3] **29**, 1200 (1903). Bailey and Lochte, THIS JOURNAL, **39**, 2443 (1917).