

The unsaturated hydrocarbon (5.9 g.) is heated with sulfur (2 g.) at 250° until no more hydrogen sulfide is evolved (one hour) and then distilled. There is obtained 4.5 g. of *o,m'*-ditolyl boiling at 265–267°.

**1-Benzoylfluorenone.**—The *o,m'*-ditolyl (4 g.) on oxidation with potassium permanganate gives 2.3 g. of *iso*-diphenic acid (m. p. 215–216°) and this is converted into fluorenone-1-carboxylic acid (m. p. 191–193°) by treatment with sulfuric acid.<sup>9</sup>

Fluorenone-1-carboxylic acid (0.35 g.) is refluxed with an excess of thionyl chloride for one hour and then warmed under reduced pressure. The crystalline acid chloride remaining is dissolved in 10 ml. of benzene, and 0.5 g. of aluminum chloride is added. After it has been warmed on a water-bath for ten minutes, the mixture is hydrolyzed with ice and hydrochloric acid. The benzene solution is separated and the solvent is distilled under reduced pressure. The residue is crystallized from alcohol, when there is obtained 0.2 g. of 1-benzoylfluorenone in the form of yellow needles that melt at 114–116°. The compound gives a red-brown color with sulfuric acid.

*Anal.* Calcd. for C<sub>20</sub>H<sub>12</sub>O<sub>2</sub>: C, 83.8; H, 4.2. Found: C, 84.2; H, 4.3.

### Summary

The halochromic sulfate of  $\alpha,\gamma$ -bisdiphenylene- $\beta$ -phenylallyl alcohol decomposes in acetic acid solution to give 1-diphenylene-2-phenyl-3,4-phenyleneindene, a hydrocarbon which contains a ring system hitherto considered impossible.

The structure of this hydrocarbon is proved by its degradation through 1-diphenyleneoxymethylfluorenone and *o*-(fluorenone-1-carbonyl)-benzoic acid to 1-benzoylfluorenone.

An independent synthesis of 1-benzoylfluorenone is described.

<sup>9</sup> Mayer and Freitag, *Ber.*, **54**, 354 (1921).

CAMBRIDGE, MASSACHUSETTS

---

## COMMUNICATIONS TO THE EDITOR

### THE PREPARATION OF *l*-ARABINOSE AND *l*-RIBOSE BY THE OXIDATION OF *l*-ARABINAL WITH BENZOIC PERACID

*Sir:*

By the reactions *l*-arabinose  $\longrightarrow$  acetobromo-*l*-arabinose  $\longrightarrow$  diacetyl-*l*-arabinal  $\longrightarrow$  *l*-arabinal, employed by Gehrke and Aicher [*Ber.*, **60**, 918 (1927)] and by Meisenheimer and Jung [*ibid.*, **60**, 1462 (1927)] we have prepared 75 g. of crystalline *l*-arabinal, with melting point 78–81° and  $[\alpha]_D^{20-25} -192^\circ$ , in chloroform. An aqueous solution of 68 g. of this *l*-arabinal was stirred with a solution of benzoic peracid in ethyl acetate according to the general procedure of Levene and Tipson [*J. Biol. Chem.*, **93**, 631 (1931)]. The titration with iodine by the directions of Goebel [*ibid.*, **72**, 801 (1927)] was then equivalent to the oxidation of 78% of the *l*-arabinal to aldopentose. The observed rotation of the solution gave, on the basis of the above yield of aldopentose, the value  $[\alpha]_D^{20-25} +49.77^\circ$ . This rotation has now been shown to be due largely to the presence of both *l*-arabinose and *l*-ribose in the reaction product.

The solution of the above reaction products was concentrated to a sirup, thinned with absolute alcohol and ether, and yielded 7 g. of crystalline *l*-arabinose. This sugar was recrystallized to 5.5 g. of pure *l*-arabinose, with m. p. 159–160° and  $[\alpha]_D^{20-25} +104.6^\circ$ , in water. The solution containing the remaining larger portion of the reaction products was again concentrated to a sirup, from which no more *l*-arabinose could be crystallized. After three weeks crystal nuclei appeared spontaneously in this sirup. These were stirred into the sirup after the addition of absolute alcohol. Refrigeration overnight resulted in the formation of 15 g. of crystalline *l*-ribose, with m. p. 81–84° and  $[\alpha]_D^{20-25} +23.85^\circ$  (seventeen hours after solution in water). One recrystallization from absolute alcohol has raised its melting point to 85–87°. From the mother liquors an additional 13 g. of *l*-ribose has been secured by direct crystallization, and 8.7 g. more by way of the *p*-bromophenylhydrazone in the method of van Ekenstein and Blanksma [*Chem. Weekblad*, **22**, 373 (1909)]. The purified *p*-bromophenylhydrazone of *l*-ribose melted at 171–172°, while the value given by Levene and Jacobs [*Ber.*, **42**, 2474 (1909)] for the same derivative of *d*-ribose was 170°.

The synthesis of both *d*- and *l*-ribose may now be accomplished by the above reactions more quickly and cheaply than by preparations from any other sources. Our studies, which were supported in part by a Grant-in-aid from the National Research Council, will be more fully described in a future publication.

From the *l*-ribose which has thus been formed we shall undertake the preparation, by the cyanhydrin reaction, of the remaining unknown aldohexoses, *l*-allose and *l*-altrose.

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY  
LOYOLA UNIVERSITY SCHOOL OF MEDICINE  
CHICAGO, ILLINOIS

RECEIVED OCTOBER 19, 1932  
PUBLISHED DECEMBER 13, 1932

W. C. AUSTIN  
FRED L. HUMOLLER

## THE FLUOROCHLORIDES OF SILICON

Sir:

Since 1915 this Laboratory has been engaged in the investigation of the fluorides, especially in Groups III and IV of the periodic table.<sup>1</sup> Unaware of any other investigators working on the problem, we have continued the studies begun in this Laboratory some time ago on the fluorination of

<sup>1</sup> Germann and Booth, *J. Phys. Chem.*, **21**, 92 (1917); Germann and Cleaveland, *Science*, [2] **53**, 582 (1921); Germann and Torrey, *ibid.*, **54**, 16 (1921); Germann and Booth, *J. Phys. Chem.*, **30**, 369 (1926); Booth and Starrs, *ibid.*, **35**, 3553 (1931); Booth and Carter, *ibid.*, **36**, 1359 (1932); Booth, Mong and Burchfield, *Ind. Eng. Chem.*, **24**, 328 (1932); Booth and Bixby, *ibid.*, **24**, 637 (1932); Booth, Swinehart and Morris, *THIS JOURNAL*, **54**, 2561 (1932).

halides and have prepared the compounds  $\text{SiFCl}_3$ ,  $\text{SiF}_2\text{Cl}_2$ ,  $\text{SiF}_3\text{Cl}$  by the direct method of the reaction of antimony trifluoride on silicon tetrachloride in the presence of either antimony pentachloride, chlorine or similar catalyst, obtaining large quantities of these products very readily along with lesser amounts of silicon tetrafluoride.

Recently in an excellent paper Schumb and Gamble<sup>2</sup> have obtained the last three of these compounds, that is,  $\text{SiF}_2\text{Cl}_2$ ,  $\text{SiF}_3\text{Cl}$  and  $\text{SiF}_4$  by the indirect method of the more difficult explosive reaction of chlorine on  $\text{Si}_2\text{F}_6$  at elevated temperatures. However, our method permits ready control of the product obtained, that is, the fluorination can be made progressive by condensing the higher boiling compounds, for instance the  $\text{SiFCl}_3$ , and letting them run back into the generator. By this reaction we have prepared over 200 liters of  $\text{SiFCl}_3$ , 100 liters of  $\text{SiF}_2\text{Cl}_2$  and 75 liters of  $\text{SiF}_3\text{Cl}$ . As would be expected, much larger quantities of the least fluorinated compound were obtained. The boiling points of  $\text{SiF}_2\text{Cl}_2$  and  $\text{SiF}_3\text{Cl}$  observed by us agree closely with the values obtained by Schumb and Gamble.

They found a very small amount of a higher boiling material of which they say, "Because of the difficulty of purifying the small quantity of this higher boiling residue, its composition was not definitely established but it is probable that a little of the third fluorochloride,  $\text{SiFCl}_3$ , was contained therein." We have definitely prepared and purified large quantities of  $\text{SiFCl}_3$ , boiling point  $12.2^\circ$ , and established its composition.

The critical constants of these three gases have also been determined

For  $\text{SiFCl}_3$ ,  $T_c = 165.17 \pm 0.05^\circ$  and  $P_c = 34.34$  atm.

For  $\text{SiF}_2\text{Cl}_2$ ,  $T_c = 95.75 \pm 0.05^\circ$  and  $P_c = 34.57$  atm.

For  $\text{SiF}_3\text{Cl}$ ,  $T_c = 34.50 \pm 0.10^\circ$  and  $P_c = 34.42$  atm.

All these gases are completely hydrolyzed by water, yielding hydrated silica, fluosilicic and hydrochloric acids. We have found them somewhat nauseating and very irritating when inhaled. The complete data and physical and chemical properties will be reported in a subsequent article.

<sup>2</sup> Schumb and Gamble, *THIS JOURNAL*, **54**, 3943 (1932).

MORLEY CHEMICAL LABORATORY  
WESTERN RESERVE UNIVERSITY  
CLEVELAND, OHIO

HAROLD SIMMONS BOOTH  
CARL F. SWINEHART

RECEIVED OCTOBER 22, 1932  
PUBLISHED DECEMBER 13, 1932

---

## A NEW GENERAL METHOD FOR FLUORINATION OF INORGANIC HALIDES

Sir:

The fluorination of silicon chloride by antimony trifluoride with a catalyst to yield fluorochlorides and fluorides as described in the previous

note appears to be a general reaction which may be expected to proceed whenever both the fluoride and chloride (or bromide or iodide) are non-polar. With a polar fluoride it may proceed providing the mixed fluoro-halide is non-polar and volatile.

It seems further that whenever the heat of this reaction is high, or when the temperature is high, fluorination tends to go to completion but where the heat of reaction is low, or the temperature is kept down, intermediate fluorohalides are obtainable, and fluorination may be made progressive by condensing the least fluorinated compound back into the generator for further reaction. The latter is characteristic of the reaction with halides of Group IV. The reaction of  $\text{SbF}_3$  with a catalyst on  $\text{SiCl}_4$  is slower than on  $\text{CCl}_4$ , on  $\text{GeCl}_4$  slower than on  $\text{SiCl}_4$ , and slow with  $\text{SnCl}_4$ . Since both  $\text{CCl}_4$  and  $\text{SiCl}_4$  yield fluorochlorides and fluorides, the gases from  $\text{GeCl}_4$  and  $\text{SnCl}_4$  are probably likewise fluorochlorides and fluorides, especially since the reaction characteristics are precisely the same. Small amounts of gas are evolved with  $\text{TiCl}_4$ , but this may be due to impurities. In these cases we have found it advisable to increase the speed of the reaction by warming the reaction flask gently; in others it is necessary to diminish the speed of the reaction by cooling. It is always advisable to use excess of the liquid halide (or an inert solvent) to absorb the heat of reaction, thus controlling its speed.

The reaction with  $\text{PCl}_3$  or  $\text{PBr}_3$  gives a smooth evolution of gases but the reaction with  $\text{PCl}_5$  is violent. When  $\text{SbF}_3$  is added to solid  $\text{PCl}_5$ , reaction is delayed, begins slowly, gathers speed rapidly, and suddenly clouds of gases evolve, while the reaction mass liquefies. In solvents the violence of this reaction is diminished, and the gases evolved are phosphorus fluorochlorides with some  $\text{PF}_5$  and  $\text{PF}_3$ .

Non-polar oxychlorides also react with  $\text{SbF}_3$  in the presence of a catalyst to yield gases. For instance,  $\text{SeOCl}_2$ ,  $\text{SO}_2\text{Cl}_2$ , and even  $\text{VOCl}_3$  when gently warmed, evolved gases.  $\text{POCl}_3$  evolves gases immediately with  $\text{SbF}_3$  without a catalyst.

Even non-polar thiohalides react. For example,  $\text{PSCl}_3$  yields gases immediately with  $\text{SbF}_3$  without a catalyst.  $\text{SiHCl}_3$  yields fluorochlorides with  $\text{SbF}_3$  and  $\text{SbCl}_5$ , and probably  $\text{SiBr}_4$ ,  $\text{Si}_2\text{Cl}_6$ ,  $\text{Si}_3\text{Cl}_8$ ,  $\text{SiSCl}_2$ ,  $\text{Si}_2\text{OCl}_2$ ,  $\text{BCl}_3$ ,  $\text{B}_2\text{Cl}_4$ ,  $\text{POCl}$ ,  $\text{SOCl}_2$ , etc., will react similarly.

This is a simple, general method for preparing fluorohalides, and fluorides, many of which have been difficult to prepare heretofore. As far as we can find this is the first time in the forty years since Swarts [*Acad. Roy. de Belgique*, **24**, 309, 474 (1892)] discovered that  $\text{SbF}_3$  and a catalyst would cause partial replacement of a halogen in an aliphatic halide that this reaction has been successfully applied to the preparation of inorganic fluorohalides and fluorides.

Investigations are now in progress in the Laboratory on all the applica-

tions of this reaction to all the non-polar inorganic halides and will be reported as rapidly as possible.

MORLEY CHEMICAL LABORATORY  
WESTERN RESERVE UNIVERSITY  
CLEVELAND, OHIO

HAROLD SIMMONS BOOTH  
CARL F. SWINEHART

RECEIVED OCTOBER 22, 1932  
PUBLISHED DECEMBER 13, 1932

### THE ACTION OF NITROUS ACID ON PHENYL- $\alpha$ -( $\beta$ -NAPHTHOL)-AMINO-METHANE. A CORRECTION

*Sir:*

In a recent paper [Ray, THIS JOURNAL, 54, 295 (1932)] it was reported that phenyl- $\alpha$ -( $\beta$ -naphthol)-aminomethane on treatment with nitrous acid gave an aliphatic diazo compound. Subsequent work, the details of which are soon to appear, has shown that the reaction is much more complex than was originally supposed. The compound in question is not an aliphatic diazo compound but an N-nitroso derivative of a heterocyclic compound.

CHEMICAL LABORATORY  
UNIVERSITY OF CINCINNATI  
CINCINNATI, OHIO

FRANCIS EARL RAY

RECEIVED OCTOBER 31, 1932  
PUBLISHED DECEMBER 13, 1932

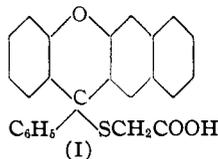
### THE ACTION OF SODIUM IN LIQUID AMMONIA ON DERIVATIVES OF OPTICALLY ACTIVE TRIARYLMETHANES

*Sir:*

In view of a recent publication by Ashley and Shriner [THIS JOURNAL, 54, 4410 (1932)] on an attempt to prepare an optically active salt of the type  $\left[ \begin{array}{c} R_2 \\ R_1 : \overset{\ominus}{C} : R_3 \end{array} \right] Na^+$  it seems advisable to place on record certain experiments which have been conducted in this Laboratory, and which were reported to the Society at its meeting in New Orleans, March 28-April 1, 1932.

In recent publications from this Laboratory a method has been described for preparing certain derivatives of optically active triarylmethanes. Investigations of such optically active compounds led us to believe that a study of their behavior toward sodium in liquid ammonia should be of special interest. For this purpose 12-phenyl-12- $\beta$ -benzoxanthenthio-glycolic acid (I), m. p., 187-188°, has been prepared.

The pure *levo* modification of this compound (m. p. 184-185°) prepared by repeated crystallization of its brucine salt gave  $[\alpha]_D^{20}$  in acetone -48.5°. This material in liquid ammonia was treated with metallic sodium



in the absence of oxygen. The deep orange-brown sodium triarylmethyl so formed was allowed to react with a slight excess

of dry solid ammonium bromide. When these reactions were carried out under suitable conditions, the corresponding colorless trisubstituted methane was found to be optically active. In one experiment a specific rotation  $[\alpha]_D^{20}$  in acetone  $-11.7^\circ$  was obtained. Since this methane derivation was obtained in an optically active condition it follows that the colored sodium triarylmethyl must have been active. Hence the three groups and the central carbon atom of the ion could not have been in a plane.

The optical stability of such an ion is being investigated further and a discussion of these results will be published at a later date.

FRICK CHEMICAL LABORATORY  
PRINCETON UNIVERSITY  
PRINCETON, NEW JERSEY

RECEIVED NOVEMBER 10, 1932  
PUBLISHED DECEMBER 13, 1932

FREDERIC H. ADAMS  
EVERETT S. WALLIS

---

#### OXIDATION COLORS DERIVED FROM 5,6-DIAMINOURACIL

*Sir:*

Ortho-, meta- and para-diamines differ in their behavior toward oxidizing agents, such as hydrogen peroxide, as follows. With ortho-diamines two molecules react to form a diaminophenazine. With para-diamines two or more molecules react to form a quinone-anil of the type of Bandrowski's base. Meta-diamines, however, do not react. Nevertheless, in the presence of an ortho- or para-diamine (which is capable of forming an ortho- or para-quinoid derivative on oxidation), meta-diamines do react to form deeply colored substances which have found application in fur and hair dyeing.

We find that 5,6-diaminouracil (an ortho-diaminopyrimidine) is also capable of reacting with meta-diamines, aminophenols and diphenols, in the presence of hydrogen peroxide, to form colored substances which dye animal fibers. Thus, for example, the following colors have been obtained from this pyrimidine: with *m*-phenylenediamine, purple; with *m*-aminophenol, old rose; with resorcinol, salmon.

CHEMICAL LABORATORIES  
COLUMBIA UNIVERSITY  
NEW YORK, N. Y.

RECEIVED NOVEMBER 11, 1932  
PUBLISHED DECEMBER 13, 1932

MARSTON TAYLOR BOGERT  
DAVID DAVIDSON

---

#### THE CONCENTRATION AT WHICH HEATS OF DILUTION ARE MEASURED IN THE CALORIMETRIC METHOD: A CORRECTION

*Sir:*

In a recent letter [THIS JOURNAL 54, 4114 (1932)] we objected to certain of the claims made by E. Lange and A. L. Robinson based upon the extrapolation of their calorimetric data for intermediate heats of dilution

to the reference state of infinite dilution. We have since discovered that our communication was based upon an interpretation of their procedure which is erroneous, namely, that a separate extrapolation was made for each pair of solutions in order to determine the heat content of the solution at each final concentration. Instead, only the value for the lowest final concentration depends entirely upon extrapolation; the values for the heat content of all other recorded concentrations being obtainable by *alternately adding* and *subtracting* the measured values for the intermediate heats of dilution. Our objections to their procedure are consequently without foundation.

DEPARTMENT OF CHEMISTRY  
COLUMBIA UNIVERSITY  
NEW YORK CITY

RECEIVED NOVEMBER 12, 1932  
PUBLISHED DECEMBER 13, 1932

VICTOR K. LA MER  
I. A. COWPERTHWAIT

---

#### ROTENONE. XXIV. SYNTHESIS OF TETRAHYDROTUBANOL

*Sir:*

As has been shown recently [Haller and LaForge, *THIS JOURNAL*, **53**, 4460 (1931); **54**, 1988 (1932)], tubaic acid ( $C_{12}H_{12}O_4$ ), obtained from rotenone by the action of alcoholic potash, is converted by drastic catalytic hydrogenation into tetrahydrotubaic acid ( $C_{12}H_{16}O_4$ ). When heated to its melting point, tetrahydrotubaic acid loses carbon dioxide and yields a crystalline product, tetrahydrotubanol ( $C_{11}H_{16}O_2$ ), which has been identified as an alkyl resorcinol. Previous work on rotenone and its derivatives indicated that the side chain is an isoamyl group. It was suggested that tetrahydrotubanol is 2,6-dihydroxy-1-isoamylbenzene. This compound has now been synthesized and found to be identical with tetrahydrotubanol. The synthesis was accomplished by the following set of reactions. 2,6-Dimethoxybenzotrile [Lobry de Bruyn, *Rec. trav. chim.*, **2**, 210 (1883)] was allowed to react with isobutylmagnesium bromide and the resulting ketimine was hydrolyzed to 2,6-dimethoxyphenyl isobutyl ketone. The ketone was reduced to 2,6-dimethoxy-1-isoamylbenzene, which on demethylation yielded 2,6-dihydroxy-1-isoamylbenzene. A comparison of its physical and optical properties with those of tetrahydrotubanol showed them to be identical. Experimental details will be presented in an early paper.

INSECTICIDE DIVISION  
BUREAU OF CHEMISTRY AND SOILS  
U. S. DEPARTMENT OF AGRICULTURE  
WASHINGTON, D. C.

H. L. HALLER

RECEIVED NOVEMBER 23, 1932  
PUBLISHED DECEMBER 13, 1932

## THE THERMAL INTERCONVERSION OF MIXED BENZOINS

Sir:

The appearance of a paper by E. Margaret Luis [*J. Chem. Soc.*, 2547 (1932)] on the "Interconversion of Mixed Benzoins," and of an article by Buck and Ide [THIS JOURNAL, 54, 4359 (1932)] in which they describe attempts to effect the same interconversion, induce us to report that, in the course of certain of our experiments on the reaction of arylamines with  $\alpha$ -hydroxy and  $\alpha$ -bromo ketones, we have been able to effect the partial transformation of anisbenzoin,  $p$ - $\text{CH}_3\text{OC}_6\text{H}_4\text{CHOHCOC}_6\text{H}_5$ , into benzanisoin,  $p$ - $\text{CH}_3\text{OC}_6\text{H}_4\text{COCHOHC}_6\text{H}_5$ , by simply heating the former above its melting point. The same transformation is effected quantitatively by distillation of anisbenzoin in vacuum (1 mm.).

We have found that anisbenzoin, which we have prepared both by the method of Asahina and Terasaka [*J. Pharm. Soc. Japan*, 494, 219 (1923)] as well as by the method of McKenzie, Luis, Tiffeneau and Weill, *Bull. soc. chim.*, 45, 414 (1929)], melts at  $89^\circ$  when pure. This melting point was given by Asahina and Terasaka, while McKenzie and his collaborators give  $100$ – $101^\circ$  as the melting point. The crystals melting at  $89^\circ$  have been examined by us under the microscope and seem to be perfectly pure. We have found that through slow heating, and then subsequent cooling, of the anisbenzoin (m. p.  $89^\circ$ ) its melting point can be altered. After a number of such treatments, its melting point rises to a value approximating the melting point given by McKenzie and his collaborators. We are therefore of the opinion that the  $101^\circ$  compound of McKenzie and his co-workers is already a mixture of the benzanisoin (m. p.  $106^\circ$ ) and the anisbenzoin (m. p.  $89^\circ$ ).

DEPARTMENT OF CHEMISTRY  
HOWARD UNIVERSITY  
WASHINGTON, D. C.

RECEIVED NOVEMBER 25, 1932  
PUBLISHED DECEMBER 13, 1932

PERCY L. JULIAN  
WALTER PASSLER

---

**NEW BOOKS**

**Chemical Analysis by X-Rays and its Application.** By GEORG VON HEVESY. The George Fisher Baker Non-Resident Lectures in Chemistry at Cornell University, 1931. The McGraw-Hill Book Company, Inc., 330 West 42d Street, New York, 1932. 333 pp. Price, \$3.00.

This volume contains the lectures delivered by Professor Georg von Hevesy at Cornell University in the winter of 1931–32 during his tenure of the George Fisher Baker Non-Resident Lectureship at that institution.

The introductory lecture is entitled "The Age of the Earth." This is followed by three series of lectures, the subjects of each series being as follows: the first series, of ten lectures, "Analysis by Means of X-Rays";