was collected, washed and dried (800 mg.) and heated for one hour on a steam-bath with 10 cc. of pyridine. The solution was diluted with 100 cc. of ether, filtered from digitonin, and the filtrate was washed with dilute hydrochloric acid until acid, and then with water. The ether was evaporated to dryness and the residue was crystallized from methyl alcohol to yield 150 mg. of uranediol, m. p. 215°. It gave no depression in melting point when mixed with uranediol (213°) isolated from mares' pregnancy urine.

The acetate was prepared from this compound in the usual manner, m. p. 160°. It gave no depression in melting point when mixed with uranediol diacetate.

*Anal.* Calcd. for $C_{26}H_{40}O_4$: C, 74.4; H, 10.0. Found: C, 74.2; H, 10.1.

The filtrate from the digitonide was concentrated to 10 cc. and diluted with 100 cc. of ether to precipitate the excess digitonin. This was filtered off and the filtrate after several washings with water was evaporated to dryness and the remaining oil was found to resist crystallization. The solution was evaporated to dryness and the oily residue was converted to the acetate by refluxing it for one hour with 10 cc. of acetic anhydride and evaporating the solution in vacuum. The residue was crystallized from methyl alcohol to yield the triacetate of triol (II) m. p. 188°. It gave no depression in melting point with the triacetate of triol (II) obtained previously m. p. 192°.

**Partial Reduction of Uranetrione in Alcohol.**—A suspension of 200 mg. of platinum oxide in a solution of 300 mg. of uranetrione in 200 cc. of ethyl alcohol and 100 cc. of ether was shaken with hydrogen at 3 atmospheres and 25° for one hour and then filtered from the catalyst. The filtrate was distilled to remove the ether and then added to a solution of 2 g. of digitonin and allowed to stand for eight hours. The digitonide (200 mg.) was decomposed as usual, giving 50 mg. of white solid which was purified by crystallization from methyl alcohol, m. p. 225° (fibrous clusters).

*Anal.* Calcd. for $C_{21}H_{32}O_3$: C, 75.8; H, 9.7. Found: C, 76.0; H, 9.7.

A portion of this compound was converted to the acetate which melted at 250° (from alcohol).

*Anal.* Calcd. for $C_{23}H_{34}O_4$: C, 73.7; H, 9.2. Found: C, 73.6; H, 9.2.

**Attempted Isomerization of Uranediol.**—Uranediol (150 mg.) was dissolved in 50 cc. of xylene, 2 g. of sodium was added and the mixture was refluxed for nine hours. The recovered product was dissolved in 50 cc. of ethyl alcohol and treated with 2 g. of digitonin. The digitonide was filtered off, dried and heated in pyridine for one hour. The solution was diluted with ether and filtered, and the filtrate yielded on evaporation a product which on crystallization from acetone gave 100 mg. of the original uranediol, m. p. 214°. The portion not precipitated by digitonin could not be crystallized to a pure product.

The authors wish to express their thanks to Parke, Davis & Co. of Detroit, Michigan, for a grant of funds supporting this work.

## Summary

The reduction products of uranetrione were studied and found to be uranediol, a new triol and uranol-3β-dione-11,20.

STATE COLLEGE, PENNA. RECEIVED APRIL 13, 1938

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

# A New Fluorination Method

BY ALBERT L. HENNE

**Principle of the Method.**—This paper reports the use of nascent mercuric fluoride as a method for replacing one or several halogen atoms by fluorine in various types of compounds. In practice, the method consists in passing a stream of hydrogen fluoride through a well-stirred mixture of mercuric oxide and the substance to be fluorinated. The reaction between the acid and the oxide occurs instantly, and so also does the one between the mercuric fluoride so generated and the organic material. Since a great deal of heat is evolved, means must be provided to prevent the reaction from escaping control, and also to avoid the loss of volatile or easily destroyed reaction products. These means vary with the substances undergoing fluorination and therefore merely call for some ingenuity.

**Dry and Nascent Mercuric Fluoride.**—The use of anhydrous mercuric fluoride as a fluorinating agent has been described before.[1] It was pointed out at the time that only the anhydrous salt could be used, and this statement was verified repeatedly. Attempts to manufacture the dry salt by methods more conventional than the action of fluorine upon mercuric chloride forced the conclusion that aqueous reagents invariably would yield a dihydrated salt which could not be converted to the anhydrous salt because it always would lose hydrofluoric acid in preference to water. In an effort to circumvent this, mercuric oxide and hydrogen fluoride were allowed to react in an inert organic liquid. This reaction generates one molecule of mercuric fluoride and only one

---

(1) Henne and Midgley, THIS JOURNAL, **58**, 884 (1936).

molecule of water, or possibly the monohydrated salt, and it was hoped that this monohydrate in contrast to the dihydrate might be dried to the anhydrous salt. Methylene chloride and chloroform were chosen as reaction media because organic chlorides are not appreciably affected by mercuric fluoride at room temperature, because their low boiling points would automatically maintain the reaction at 40 or 60°, respectively, and because it was hoped that their high densities might cause the water to separate in a top layer. The result of the experiments, however, was quite unexpected, because the white crystalline salt thus obtained was pure mercuric chloride, instead of fluoride, an indication that the nascent mercuric fluoride had reacted instantly with the organic chloride despite the low temperature and the presence of water. An examination of the volatilized reaction products disclosed the presence of methylene fluoride and difluorochloromethane, respectively, two substances described in a preceding paper.[2] This confirmed the interpretation of the reaction course.

**Practical Adaptation.**—The fluorination of acetylene tetrabromide was studied quantitatively to supply a gage of the practical work of this new fluorination method, and the following simple procedure was found convenient for laboratory operation.

Three gram molecules of acetylene tetrabromide was placed in a tall metal container, preferably made of nickel, and cooled externally with water. One gram molecule of red mercuric oxide was added to the liquid, and immediately stirred to prevent the formation of a heavy paste or cake. Dry hydrogen fluoride from a commercial cylinder was led into the liquid through a metal tube (flexible copper tubing is convenient). The flow of gas was regulated so that the temperature of the reaction mixture never exceeded 40 to 50°. The red color of the mercuric oxide fades progressively to pink, yellow, grayish white and finally to gleaming white; this is the end of the reaction. At this point it was found that about 2.3 gram molecules of hydrogen fluoride had been used, which is an excess of 15% over the theoretical quantity required. The white salt is pure mercuric bromide, with a correct mercury content of 55.6%. It may be noted that an aqueous layer of concentrated hydrofluoric acid floats on the surface. At the end of the reaction the mixture was poured onto cracked ice and washed roughly by decantation to remove the excess of acid. It was then placed in a distilling flask, with twice its volume of water, and heated with a free flame, kept in constant motion to prevent foaming. Steam distillation of the fluorinated material takes place promptly and carries along some acetylene tetrabromide. The distillate was decanted from the water, dried and rectified; it yielded 0.6 gram molecule of $CHF_2CHBr_2$ and 0.4 gram molecule of $CHFBrCH_2Br$, which is an 80% fluorination yield, based on the mercuric oxide. The material left unsteamed in the distilling flask was cooled overnight, preferably on ice; this causes the mercuric bromide to crystallize out completely and facilitates filtration. The aqueous layer was separated as completely as practical, and the remainder filtered with suction and air dried on the filter. The filtrate separates into a layer of acetylene tetrabromide and a layer of water. The solid material was removed from the filter, placed in a bottle, covered with chloroform, vigorously shaken for twenty minutes, and then filtered by suction. Pure mercuric bromide is left on the filter, while the filtrate is a chloroform solution containing from 75 to 100 cc. of acetylene tetrabromide. Distillation of the chloroform makes it possible to recover the latter material.

**Mercury Recovery.**—As described so far, this method would be quite costly if the mercury could not be recovered and reoperated. This, however, was performed as follows. The mercury bromide was dropped in small quantities into an aqueous solution of sodium hydroxide. A great deal of heat was evolved, and a black precipitate of mercury oxides was generated, which settled very slowly. The mixture was brought to boiling, then allowed to settle overnight. After decantation of the aqueous layer, water was added and brought to boiling. After again settling overnight the liquid was decanted from the black substance which was then allowed to dry in air, after which it was placed in a steel container (made of pipe fittings), equipped with a screw cap and a delivery tube leading into a pan of water. The steel container was heated with a large gas burner to decompose the mercury oxides and distil the mercury into the water. More mercury was recovered by pouring the distillation residue into water. The recovery of the mercury is quite complete when large enough quantities are used in each batch to avoid mechanical losses.

**Temperature and Yields.**—The new reaction was then applied to the fluorination of $CH_2BrCHBr_2$, and it was found that $CHFBrCH_2Br$ and $CHF_2CH_2Br$ were generated, as expected, but the fluorination yield of about 30% was at first disconcerting. The mercury bromide was recovered quantitatively, but the tribromoethane was not, and its loss corresponded to the missing fluorinated material. The reaction was tried at different temperatures and it was promptly found that the yield improved as the temperature was lowered. At 0° the yields increased to 50%, and at −20° the yields became about 65 to 70%. This showed that the yield is mostly a matter of adequate temperature control.

**Generality of the Reaction.**—In order to test the generality of the reaction, the new method was applied to different compounds, at room temperature, with and without saturated hydrocarbons as diluents. Fluorination always occurred instantly and yields were obtained even on small batches and without many precautions, which were always considerably higher than 50%, usually about 70%. More careful handling, tried in only a few cases, always improved the yields markedly. The results were as follows: $AcOCH_2CH_2F$ was obtained from $AcOCH_2CH_2Br$; $AcOCH_2CHF_2$ from $AcOCH_2CHBr_2$; $CH_2F_2$ from $CH_2Cl_2$; $CHClF_2$ from $CHCl_3$; $CH_3CHF_2$ from $CH_3CHCl_2$; $CH_3(CH_2)_5CHF_2$ from $CH_3(CH_2)_5CHCl_2$; $(C_6H_5)_2CF_2$ from $C_6H_5CCl_2$; $(C_6H_5)_3CF$ from $(C_6H_5)_3CCl$; $CF_2ClCF_2Cl$ from $CFCl_2CFCl_2$, $CHF_2CClF_2$ from $CHCl_2CClF_2$ and

---

(2) Henne, THIS JOURNAL, **59**, 1400 (1937).

from CHF$_2$CCl$_3$. In no case was the fluorination reaction accompanied by loss of hydrogen chloride or hydrogen fluoride and consequently no ethylenic by-product was found. There was usually no tar formation, but a very small quantity was formed in the worst cases, when reagents of "technical" grade were employed.

## Summary

A method of fluorination is described which consists in passing a stream of hydrogen fluoride through a mixture of the substance to be fluorinated and mercuric oxide. Practical directions are given for obtaining good yields and for a simple method of recovering the mercury.

THE MIDGLEY FOUNDATION
COLUMBUS, OHIO

RECEIVED APRIL 1, 1938

---

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICS, HARVARD UNIVERSITY]

# Variations in the Relative Abundances of the Isotopes of Common Lead from Various Sources

BY ALFRED O. NIER[1]

Because of the apparently constant atomic weight of common or ore lead, the assumption usually has been made that its isotopic composition also is constant. Whereas several isolated isotopic analyses of common lead have been made, there is no record of any systematic study having been undertaken for the purpose of checking the constancy of the relative abundances. In the present work twelve samples were studied with a mass spectrometer and considerable variations were found. The investigation is of particular interest, as the specimens examined vary greatly in both geologic age and geographic origin. Moreover, of the twelve samples, nine have had chemical atomic weight determinations made on them—all in the same laboratory.

**Apparatus and Procedure.**—The mass spectrometer used for obtaining the results to be presented here already has been described.[2] Positive ions of lead are formed by the collision of electrons with lead iodide vapor. The ions are drawn out of the region where they are formed, are accelerated and sent around a 180° magnetic analyzer where the ion currents are measured with an electrometer tube amplifier.

During an analysis, the portion of the tube containing the semicircular analyzer is kept at room temperature. The part where the ions are formed is held around 400°, and the side-tube from which the lead iodide vapor diffuses into the ionizing region is maintained at approximately 300°, the exact temperature depending on the pressure desired in the ionizing region. In actual practice, this pressure was between $10^{-4}$ and $10^{-5}$ mm. The amount of material needed for an analysis is very small. During a typical run, where no attempt was made to economize on material, less than 13 mg. of lead iodide, *i. e.*, less than 6 mg. of lead, was consumed. With reasonable care it should be possible to obtain reliable results on 1 mg. of lead.

The procedure in making an analysis was as follows: the sample to be studied was attached in the evening and the mass spectrometer tube evacuated and baked overnight in order thoroughly to out-gas it. Measurements were taken the next morning and afternoon. The side-tube containing the sample was removed and the mass spectrometer was again baked overnight, this time to remove the lead iodide. The following morning the apparatus was baked for several hours with iodine vapor flowing through it to combine with any metallic lead deposited in the tube from the thermal decomposition of lead iodide. Baking of the tube continued until late in the evening in order to remove the remaining traces of lead iodide. A new sample could then be attached and the procedure repeated. It is seen that an analysis may be performed every two days. Actually, in one case, fifteen samples were examined in thirty-four consecutive days.

Because of the careful treatment of the apparatus between samples, described above, the relative abundances of the isotopes obtained for a given specimen did not depend upon the previous history of the apparatus. That is to say, there was no contamination due to previous samples. In fact, one even could change from a sample of ordinary lead to one of radiogenic lead and then back again to the ordinary lead and reproduce the original results exactly.

The lead iodide was prepared by precipitation

---

(1) National Research Fellow.

(2) Nier, *Phys. Rev.*, **52**, 933 (1937).