

methyl sulfate, butyl bromide and *iso*-amyl iodide we obtained only a recovery of the original acetylonyl-barbituric acid. The comparative ease with which chloro-acetone reacted with ethylbarbituric acid suggests the possibility of preparing homologs by introducing the acetylonyl group into homologous alkyl barbituric acids.

Four of the above derivatives, diacetylonyl-, acetylonyl-benzyl-, acetylonyl-ethyl-, and acetylonyl-allylbarbituric acids were subjected to physiological test. Intraperitoneal injection in white mice of solutions in dilute alkali in amounts representing the effective dose of veronal produced no noticeable effect. Three times this dosage in the case of acetylonyl-ethyl gave after one hour the characteristic symptoms of muscular incoördination which lasted about two hours, after which recovery began without any approach to the stage of unconsciousness. The hypnotic action is therefore less than one-third that of veronal.

Summary

The acetylonyl group may be substituted directly on the 5-carbon atom of barbituric acid by means of chloro-acetone. Further substitution by halogen is readily effected, or by allyl, benzyl and acetylonyl. The less reactive alkyl halides as butyl bromide, do not react readily with acetylonyl-barbituric acid, but the acetylonyl and alkyl groups may be introduced in the reverse order by treatment of the mono-alkyl barbituric acid with chloro-acetone. The acetylonyl-alkyl barbituric acids are much less effective as hypnotics than the dialkyl barbituric acids with the same length of side chains.

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THE ALKYL TITANATES

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RECEIVED NOVEMBER 12, 1923

In studying the selective activation of titania¹ it was necessary to prepare various alkyl titanates (titanium alkoxides). Since the interest in these compounds is entirely apart from the work upon the causation of organic reactions by titania, their preparation and properties are presented in advance of the latter. The tetramethyl-, -ethyl-, -*isopropyl*-, and *N*-butyl titanates have been prepared for the first time. Demarçay² believed that he obtained the tetra-ethyl ester but we have found that he was in error. His compound was a solid, crystallized from alcohol, while the true tetra-ethyl titanate is a colorless liquid that may be distilled at 145°

¹ Compare Adkins, *THIS JOURNAL*, **44**, 2175 (1922).

² Demarçay, *Compt. rend.*, **80**, 51 (1875).

(8.5 mm). He ascribed the fact that his analysis did not agree with the calculated values for the tetra-ethyl ester to the presence of titania. We have prepared his compound and find that the analyses for titania and alcohol and the solubility of the compound show that it contains no titania but that it is in reality a mixture of oxy-ethyl titanates. There are formed oxy and hydroxy titanates, $\text{TiO}(\text{OH})(\text{OC}_2\text{H}_5)$, mono-ethyl metatitanate; $\text{TiO}(\text{OC}_2\text{H}_5)_2$, ethyl metatitanate; $\text{Ti}_2\text{O}(\text{OC}_2\text{H}_5)_6$, ethyl di-orthotitanate, and probably others.³ These are crystalline and soluble in organic solvents, the solubility increasing as the normal ester is approached. The oxy titanates crystallize from tetra-ethyl titanate when the latter is very slowly hydrolyzed.

The tetramethyl titanate is a white solid, crystallizing at 209–210°. The *isopropyl* and *N*-butyl esters are like the ethyl in that they are colorless liquids having a density near that of water. All of the tetra-alkyl esters may be distilled.

Demarçay allowed titanium tetrachloride to react with absolute alcohol to give the substance $\text{TiCl}(\text{OC}_2\text{H}_5)_3 \cdot \text{HCl}$. This was then treated with sodium ethoxide. The method is not good in that titanium tetrachloride reacts with the alcohol to give some ethyl chloride and water. All of the alkyl titanates react instantly with water so that the latter hydrolyzes the esters to a certain extent and hence Demarçay obtained oxy esters. He overlooked the small yield of the true tetra-ethyl ester in the mother liquor from which his oxy titanates crystallized. We have prepared the normal esters by the reaction of one molecular equivalent of titanium tetrachloride with four of a sodium alkoxide in alcoholic solution. The yields of esters are good when the conditions as to concentration of reagents and time of reaction are carefully controlled.

An interesting case of a quantitative alcoholysis occurs when ethyl titanate is boiled two or three times with absolute methyl alcohol, pure methyl titanate being* obtained.

Experimental Part

Tetra-ethyl Titanate.—Seventy-eight cc. of titanium tetrachloride was added during the course of two hours to a liter of absolute alcohol to which 67 g. of sodium had been previously added. The reaction flask was kept in an ice-bath and frequently shaken. After the addition of the titanium tetrachloride the mixture was refluxed for three hours and the excess of alcohol distilled. The residue was distilled from an oil-bath under a pressure of about 10 mm. The distillate below 140° was discarded. The higher-boiling distillate was freed from alcohol by heating it in a bath at 140° under reduced pressure and redistilling it; yield, 67%. The boiling point of the colorless liquid was 205° (156 mm.) or 145° (8.5 mm.); d_{20}^{20} , 1.107. It was soluble in alcohol, benzene and

³ It is interesting to note that while triethyl aluminate shows no intermediate products upon hydrolysis [Child and Adkins, *THIS JOURNAL*, **45**, 3015 (1923)] the tetra-ethyl titanate gives a series of oxy esters when similarly treated.

fractol.⁴ Titania was determined by hydrolysis, filtration and ignition, and alcohol by distillation and determination of the density of the distillate.

Analysis. Calc. for $\text{Ti}(\text{OC}_2\text{H}_5)_4$: TiO_2 , 35.1; $\text{C}_2\text{H}_5\text{OH}$, 80.7. Found: TiO_2 , 35.0; $\text{C}_2\text{H}_5\text{OH}$, 80.9.

Tetra-*isopropyl* Titanate.—Seventy-four g. of sodium, 1500 cc. of absolute *isopropyl* alcohol and 85 cc. of titanium tetrachloride were used. The reaction is slow and the mixture was refluxed for several hours. It was not possible to remove the alcohol by distillation under reduced pressure. The product was repeatedly fractionated at atmospheric pressure. A constant-boiling mixture was obtained at 230° and 740 mm. The product contained 27.0% of titanium dioxide equivalent (calc., 28.2%) indicating the presence of 4% of *isopropyl* alcohol in the ester. There was a slight decomposition on distillation at atmospheric pressure.

Tetra-*n*-butyl Titanate.—This compound was prepared as was the ethyl except that 60 g. of sodium, 1200 cc. of butyl alcohol and 69 cc. of titanium tetrachloride were used. The oil-bath in the first distillation was held at 250° and for the later removal of alcohol at 160°; yield, 80%; b. p., 185–187° (10–11 mm.); d_{20}^{20} , 0.993. The compound was a colorless liquid and was soluble in benzene, fractol, butyl alcohol and ethyl alcohol.

Analysis. Calc. for $\text{Ti}(\text{OC}_4\text{H}_9)_4$: TiO_2 , 23.5. Found: 23.2.

Tetramethyl Titanate.—One hundred g. of sodium, 1200 cc. of absolute alcohol, and 117 cc. of titanium tetrachloride were used. The reaction is very violent and the titanium tetrachloride must be added very slowly during the course of three hours while the mixture is thoroughly cooled in ice water. The methyl alcohol was distilled after an hour's refluxing. The titanate was distilled under 52mm. pressure (or less) as rapidly as possible from a bath held at 300°; yield, 40%; "crystallizing point" 209–210° (corr.); b. p., 243° (corr.) (52 mm.). The compound was a white solid slightly soluble in methyl alcohol and insoluble in fractol. The melting point is not easily determined on account of the rapidity of hydrolysis in air.

Analyses. Calc. for $\text{Ti}(\text{OCH}_3)_4$: TiO_2 , 46.5; CH_3OH , 74.4. Found: TiO_2 , 436; CH_3OH , 74.9.

Tetramethyl Titanate by Alcoholysis.—Five g. of tetra-ethyl titanate was boiled with 30 cc. of anhydrous methyl alcohol. The alcohol was then distilled and a fresh supply added. Upon the repetition of this operation pure tetramethyl titanate was obtained. *isopropyl* and *n*-butyl titanates undergo a similar alcoholysis. This is a convenient method for making the methyl derivative, since the direct method of preparation gives a low yield.

The Method of Demarçay and the Oxy-ethyl Titanates.—The compound, $\text{TiCl}(\text{OC}_2\text{H}_5)_3\text{HCl}$, a white amorphous powder, was obtained by the action of titanium tetrachloride upon absolute ethyl alcohol; 27.0% of chlorine (calc. 27.8%) was found in our product. An amount of sodium ethoxide equivalent to the chlorine content was added to the substance in an absolute alcohol solution. The mixture was refluxed for an hour, the supernatant liquid siphoned off and the remainder removed by filtration with suction. The salt contained 4.0 g. of titanium dioxide. Upon evaporation of the solution to half its volume 7.0 g. of crystals separated. After drying them in a desiccator for 36 hours 60.6% of titanium dioxide equivalent was found by analysis, while that calculated for the formula $\text{TiO}(\text{OH})(\text{OC}_2\text{H}_5)$ is 62.5%. The substance decomposes at 230° without melting. When the alcoholic solution was concentrated still further and allowed to stand for some months, crystals separated from the viscous mass. They were recrystallized from fractol and benzene. After they had been dried in a vacuum

⁴ Fractol is a petroleum fraction boiling at 60–100° and consisting mostly of unsaturated hydrocarbons.

they were analyzed and 43.7% of titanium dioxide and 68.3% of alcohol were found. There can be no question that these data indicate that the crystals consisted of a mixture of approximately 75% of $\text{TiO}(\text{OC}_2\text{H}_5)_2$ and 25% of $\text{Ti}_2\text{O}(\text{OC}_2\text{H}_5)_6$. The calculated percentages for $\text{Ti}_2\text{O}(\text{OC}_2\text{H}_5)_6$ are TiO_2 41.9%, alcohol 72.2%; for $\text{TiO}(\text{OC}_2\text{H}_5)_2$, TiO_2 51.9%, alcohol 59.7%; and for $\text{TiOH}(\text{OC}_2\text{H}_5)_3$, TiO_2 40.0%, alcohol 68.9%.

Tetra-ethyl titanate was obtained upon the distillation of the mother liquor from which the last crop of crystals was obtained. When Demarçay's method was applied to the preparation of butyl titanate even more unsatisfactory results were obtained than with ethyl titanate.

Summary

1. The tetramethyl, -ethyl, -isopropyl and *N*-butyl esters of titanic acid have been prepared in various ways and their properties described. All may be distilled and all are colorless liquids with the exception of the first, which is a white solid.

2. The substance described by Demarçay as tetra-ethyl titanate has been shown to be one of a series of oxy and hydroxy esters of titanic acid.

3. An example of a quantitative alcoholysis has been given in the conversion of ethyl titanate to methyl titanate.

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NEW BOOKS

The Chemistry Tangle Unravelled, being chemistry systematized on a new plan based on the works of Abegg, Kossel, and Langmuir. By FRANCIS W. GRAY, M.A., D.Sc., Senior Lecturer in Chemistry, Aberdeen University. Longmans, Green and Company, 55 Fifth Avenue, New York; 39 Paternoster Row, London, E. C. 4; Toronto; Bombay, Calcutta and Madras; 1923. x + 148 pp. 2 figs. 19 × 12.5 cm. Price \$2.00 net.

This surprising book is much better than its unfortunate title, reminiscent of a medieval alchemical treatise, would indicate. It represents a bold attempt to apply the ideas of Abegg, Kossel, Lewis and Langmuir to the whole field of inorganic chemistry, and there is no question but what these new ideas, particularly because of the fresh and deeper significance which they give to the periodic table, promise a much closer and more illuminating correlation of the properties and behaviors of the various elements and their compounds.

Naturally, a book which attempts so sweeping an application of new and still controversial ideas, presents many opportunities for criticism. Thus, it is unfortunate at this stage of the development of the subject to mention and adopt only the Langmuir hypothesis as to the structure of the outer shells of atoms. What little pertinent evidence we have, and particularly that concerned with the positions of the rare elements in the periodic table, seems to support the hypothesis of Bury and of Bohr rather than that of Langmuir. It is also unfortunate that the author does not adhere consistently to the postulate of "negative" hydrogen,