of the insecticidal action of these compounds is being made in coöperation with Dr. C. H. Richardson, Deciduous Fruit Insect Investigations, Bureau of Entomology.

Summary

1. α,α-, β,β-, γ,γ-, β,γ- and α,β-dipyridyls were reduced quantitatively to the corresponding dipiperidyls by means of hydrogen in the presence of platinum oxide catalyst. Impure α,γ-dipyridyl was also reduced to the dipiperidyl but proper purification could not be made.

2. Certain physical constants of the bases, their dinitroso and other derivatives were determined to characterize them.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

AN ORGANIC TITANOUS COMPOUND AND A NEW METHOD FOR THE PREPARATION OF SOLUTIONS OF TITANOUS SALTS

BY DONALD W. MACCORQUODALE AND HOMER ADKINS

RECEIVED MARCH 5, 1928 PUBLISHED JULY 6, 1928

Bischoff in 1923 observed that a blue colored substance insoluble in organic solvents and containing no sodium resulted from the reaction of an alcoholic solution of tetra-ethyl ortho titanate with metallic sodium. He demonstrated that the compound contained trivalent titanium and was presumably an ethyl titanite.

This crude ethyl titanite is readily prepared by converting titanium tetrachloride into tetra-ethyl ortho titanate.[1] The yield may be increased to 81% of the theoretical by centrifuging the mixture containing the sodium chloride and decanting off the alcoholic solution of the ortho titanate instead of distilling it from the salt mixture. The salt should be shaken and centrifuged twice with alcohol in order to wash out the ester. The titanate is readily purified by distillation so that it is entirely free from all metallic or acid impurities.

The trivalent titanium compound is most easily prepared by adding an alcoholic solution of ethyl titanate as rapidly as possible to a flask containing finely divided sodium, the flask being equipped with an efficient reflux condenser which in turn is equipped with a Bunsen valve. When the reaction becomes too vigorous, it is moderated by immersing the flask in an ice-bath for a moment. However, the more vigorous is the reduction, the better the yield of product, so that the reaction should be allowed to proceed as vigorously as the efficiency of the condenser will permit. The separation of the blue precipitate is best effected by centrifuging, after which the solution can be decanted and the precipitate washed by shaking up with absolute alcohol and centrifuging again. The product should be washed in this manner two or three times, after which it can be dried over concentrated sulfuric acid in an atmosphere of hydrogen or nitrogen. From 30 g. of ethyl titanate dissolved in 200 cc. of absolute alcohol, 20 g. of product may readily be obtained, using 10 g. of sodium for the reduction.

---

[1] Bischoff and Adkins, THIS JOURNAL, **46**, 257 (1924).

This dark blue amorphous solid contains from 55 to 70% as much trivalent titanium as would an equal weight of ethyl ortho titanite, $(C_2H_5)_3TiO_3$. It reduces aromatic nitro compounds to amines very readily and aromatic aldehydes to alcohols somewhat more slowly, when used in the form of a suspension in absolute alcohol. It dissolves in hydrochloric acid and in dilute sulfuric acid, forming the titanous salts.

When the dry ethyl titanite is exposed to the air it very rapidly turns olive-green and then white, the odor of acetaldehyde being very pronounced. To obtain samples for analysis the material, in alcoholic suspension, was transferred to small glass bulbs which were filled with nitrogen. The alcohol was removed by heating at 100° for one hour under a pressure of 5–10 mm. and the bulbs were then sealed off, filled with nitrogen. The results obtained were as follows. From 0.2287 g. of substance, 0.1736 g. of water and 0.3368 g. of carbon dioxide were obtained: calcd. for $C_6H_{15}O_3Ti$: C, 39.31; H, 8.25. Found: C, 40.18; 8.49.

Trivalent titanium was determined by titrating the ferrous salt formed by the action of the compound on an excess of ferric alum in an atmosphere of carbon dioxide. All values for trivalent titanium were low. A sample which had been boiled with absolute alcohol in a current of hydrogen for several hours showed 21.31 and 20.77% of trivalent titanium instead of the theoretical 26.25%. This would correspond to a mixture of about 80% of ethyl titanite ($(C_2H_5)_3TiO_3$) and 20% of ethyl titanate ($(C_2H_5)_4TiO_4$). Accordingly, a determination of total titanium was made by dissolving the material in concentrated hydrochloric acid with the addition of a few drops of concentrated nitric acid and precipitating the titanium as titanium dioxide.[2] The results were 24.93 and 24.86% of titanium as compared with the theoretical value of 25.21% calculated for this mixture.

From this analysis it seemed probable that the material was a mixture of the two esters and a further effort was made to effect their separation. It was found impossible to wash out the ethyl titanate but a partial separation was accomplished by heating at 156° and 8–10 mm. for one hour. Under these conditions some of the ethyl titanate distilled out and was condensed in the cold part of the tube. A sample treated in this manner was found to contain 22.85% of trivalent titanium, which corresponds to 87.4% of ethyl titanite in the preparation. Increasing the temperature from 156 to 185° had no effect. Probably the remaining impurity was in part titanium dioxide but we were unable to remove this as we found no non-reactive solvent for the ethyl titanite. It appears probable that if the titanites of the higher alcohols were prepared they would be found to be more soluble and so might be more readily purified, but this has not been attempted.

Summary

An organic trivalent titanium compound has been prepared in an impure state by the reduction with sodium of an alcohol solution of tetra-ethyl titanate. This dark blue compound acts as a reducing agent and also dissolves in hydrochloric or dilute sulfuric acid to form titanous salts. The titanous salt solutions so obtained are entirely free from iron or other metallic or acidic impurities. An improvement in the method of preparation of tetra-ethyl titanate has been described.

MADISON, WISCONSIN

---

[2] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand and Co., New York, 3d ed., **1922**, p. 542.