# DIPIPERIDYLS[1]

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There are six possible dipiperidyls corresponding to the six dipyridyls. All of the dipyridyls[3] are known, but up to the time of these experiments only three of the dipiperidyls had been prepared. The author has prepared two additional dipiperidyls, β,γ- and β,β-, leaving only the α,γ-derivative for further study.

The method of preparation is that of reduction of the dipyridyls by means of hydrogen in the presence of platinum oxide catalyst. The dipiperidyl is produced in a state of purity equal to that of the dipyridyl. Often it can be purified by suitable means when the dipyridyl cannot be easily purified.

The three dipiperidyls previously known were prepared by means of sodium and ethyl or amyl alcohol reduction and required considerable purification. γ,γ-Dipiperidyl[4] was the first dipiperidyl to be prepared by the sodium reduction and presented considerable difficulty in its purification. Ahrens prepared the dipiperidyl in a pure condition by means of the dinitroso derivative. Blau prepared α,β-dipiperidyl[5] with great difficulty, using steam distillation, crystallization of the hydrochloride from alcohol, distillation of the base and repeating the operations until a maximum melting point (68–69°) was obtained. α,α-Dipiperidyl[6] also was prepared in a pure form by Blau and required almost as much manipulation as γ,γ-dipiperidyl.

The author has prepared the dipiperidyls mentioned, together with β,γ- and β,β-dipiperidyls and also certain derivatives useful for characterizing them. All the dipiperidyls are strong bases which absorb carbon dioxide readily from the air. They are very stable to the action of heat and air. The picrates usually melt with decomposition. The bases may be titrated with two molecular equivalents of strong acid to one of base, phenolphthalein being used as indicator. The bases are very soluble in water, slightly soluble in ether and almost insoluble in petroleum ether.

In no instance does a partial reduction of the dipyridyl molecule appear to take place, either in hydrochloric acid solutions of various strengths, acetic acid solution or various solvents. The reduction goes to completion, calculated as for the formation of dipiperidyl, and stops. When

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[3] Smith, This Journal, **46**, 414 (1924).

[4] Ahrens, *Ber.*, **24**, 1479 (1891).

[5] Blau, *Monatsh.*, **13**, 330 (1892).

[6] Blau, *ibid.*, **10**, 375 (1889).

one-half this quantity is used a mixture of dipyridyl and dipiperidyl always results. In alkaline solutions, or solutions without acid, no reduction takes place at all, probably because the catalyst is inactive or rendered so by the production of the alkaline dipiperidyl.

## Experimental

The same general procedure was used in the preparation of each of the dipiperidyls. The dipyridyls were usually dissolved in a moderate excess of hydrochloric acid in water or alcoholic solution and reduced at atmospheric or higher pressures. The quantity of hydrogen absorbed agreed with the absorption of twelve hydrogen atoms. The platinum oxide catalyst was prepared by the method of Vorhees and Adams.[7] After reduction the solution was separated from the platinum, evaporated to low volume and precipitated by means of absolute alcohol as the dihydrochloride. (If the original dipyridyls were somewhat impure this precipitation effected a purification but is otherwise unnecessary for the preparation of the bases.)

The bases were freed with caustic potash and extracted with ether. They may be recrystallized from petroleum ether or a mixture of ether and petroleum ether.

The experimental results on five dipiperidyls are given in tabulated form. Only a small amount of crude $\alpha,\gamma$-dipyridyl was obtained, boiling at 282–284°, from a large quantity of mixed dipyridyls obtained in the action of sodium on pyridine. The correct quantity of hydrogen was absorbed but the dipiperidyl was too impure to prepare pure derivatives. Further study is required to obtain these $\alpha,\gamma$-derivatives.

The phenyl isothiocyanate addition products of the type $C_{10}H_{20}N_2 \cdot 2C_6H_5NCS$ crystallize well from alcohol or alcohol and water mixtures.

TABLE I

DIPIPERIDYL DERIVATIVES

| | Melting point, ° C. | | | B. pt., base, °C. | C in base, % | H in base, % | N in Dinitroso, % | S in PhNCS, % |
|---|---|---|---|---|---|---|---|---|
| | Base | Dinitroso | PhNCS comp. | | | | | |
| $\gamma,\gamma$[a] | 172 | 149 | 225[b] | .. | ... | ... | ... | 14.74 |
| | | 150 | 229 | | | | | |
| $\alpha,\alpha$[c] | Liq. | 159 | 178[d] | 259 | ... | ... | 24.20 | 14.47 |
| $\alpha,\beta$[c] | 68 | 88 | .. | 269 | ... | ... | ... | ... |
| | 69 | | | | | | | |
| $\beta,\beta$[e] | 105 | 102 | 200 | 282 | 71.09 | 11.83 | 24.93 | 14.49 |
| $\beta,\gamma$[f] | 159 | 149 | 202 | 270 | 70.90 | 11.85 | 25.30 | 14.57 |
| | | | Calculated | | 71.40 | 11.90 | 24.78 | 14.64 |

[a] Ahrens gives 160° for base and 141–143° for dinitroso compound. Base sublimes long needles below melting point, and boiling point could not be determined.

[b] Needles.

[c] Figures are identical with those given by Blau. The $\alpha,\beta$-dipiperidyl picrate, however, melted at 224°, unchanged on recrystallization. Blau gives 215°.

[d] Needles.

[e] Needles arranged in rosets.

[f] Sublimes to needles in rosets. Picrate blackens at 200° but does not melt at 230°. The platinum double chloride turns gray at 235° but does not melt at 250°. N in base, calcd., 16.7%; found, 16.8%.

The dipiperidyls resemble nicotine and hexahydronicotine in their chemical structure to a degree which makes it desirable to examine their toxicity to insects. A study

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[7] Vorhees with Adams, THIS JOURNAL, **44**, 1397 (1922).

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. $\alpha,\alpha$-, $\beta,\beta$-, $\gamma,\gamma$-, $\beta,\gamma$- and $\alpha,\beta$-dipyridyls were reduced quantitatively to the corresponding dipiperidyls by means of hydrogen in the presence of platinum oxide catalyst. Impure $\alpha,\gamma$-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.

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[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

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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.

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