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R. L. Shriner  
*State University of Iowa*

R. E. Schaeffer  
*State University of Iowa*

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## Synthesis of 4-Piperidinoflavan

By R. L. SHRINER AND R. E. SCHAEFFER

A study of the reaction of flavylum perchlorate with piperidine showed that piperidine perchlorate was formed plus two other compounds. One of these appears to be 4-piperidinoflavene which should be reducible to 4-piperidinoflavan. This compound had not been described previously, hence its synthesis was undertaken.

Flavanone was prepared according to the method of Kostanecki (1). Catalytic reduction of flavanone with hydrogen and a platinum catalyst gave a 79% yield of a compound melting at 145-147°. This corresponds to the  $\beta$ -isomer of 4-hydroxyflavan originally obtained by Karrar, Yen and Reichstein (2) as the result of a titanous chloride reduction of flavanone. Mozingo and Adkins (3) also obtained this  $\beta$ -isomer by catalytic reduction of flavanone but used copper-chromium oxide at 120° and hydrogen at 100-200 atm. Treatment of the 4-hydroxyflavan with phosphorus tribromide at 0° gave a 52% yield of 4-bromoflavan. An ether solution of this bromo-compound reacted with two equivalents of piperidine to form piperidinium hydrobromide and  $\beta$ -4 piperidinoflavan. Upon recrystallization from ether, colorless needles were obtained melting at 137-138° which had the correct analysis for this compound.

### EXPERIMENTAL PART

*$\beta$ -4-Hydroxyflavan.* To a solution of 11.2 g. of flavanone (1) in 150 ml. of purified 95% ethanol was added 0.2 g. of platinum oxide catalyst. The mixture was shaken with hydrogen at 3 atm. pressure for 2 hours in a pressure bottle. The catalyst was removed by filtration and the solvent distilled. The crude product (9 g.) was recrystallized from 30% ethanol and there was obtained 9 g. (79%) of white crystals of  $\beta$ -4-hydroxyflavan melting at 145-147°.

*4-Bromoflavan.* To a suspension of 5 g. of  $\beta$ -4-hydroxyflavan in 100 ml. of absolute ether, cooled to 0° was added 5.6 g. of phosphorus tribromide with good stirring. The mixture was allowed to stand 5 hours and then the ether layer was separated from the phosphorous acid layer. The ether layer was washed with water, then with three 60 ml.-portions of 5% sodium acetate solution and dried with anhydrous magnesium sulfate. Evaporation of the ether

gave the crude bromo-compound which was purified by solution in 35 ml. of absolute ether and cooling in a refrigerator at  $-5^{\circ}$ . There was obtained 3 g. (52%) of colorless needles melting at  $85-87.5^{\circ}$ .

Anal. Calcd. for  $C_{15}H_{13}OBr$ ; C, 62.29; H, 4.53.

Found: C, 61.81; H, 4.71.

*$\beta$ -4-Piperidinoflavan.* A solution of 2.5 g. of piperidine and 4 g. of 4-bromoflavan in 150 ml. of dry ether was allowed to stand at  $25^{\circ}$  for five days. At the end of this time the precipitate of piperidinium hydrobromide was removed by filtration and the ether allowed to evaporate. The residue was washed with cold ether and then with 200 ml. of cold water. The residue was dried over phosphorus pentoxide and recrystallized from absolute ether. The pure product consisted of colorless needles which melted at  $137-138^{\circ}$  and amounted to 1.5 g. (37%).

Anal. Calcd. for  $C_{20}H_{23}ON$ : C, 81.87; H, 7.90; N, 4.78.

Found: C, 81.99; H, 7.90; N, 4.34.

#### References

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- (3) Mozingo, R. and Adkins, H., J. Am. Chem. Soc., 60, 669 (1938).

DEPARTMENT OF CHEMISTRY  
STATE UNIVERSITY OF IOWA  
IOWA CITY, IOWA