on addition of *p*-nitrodiazobenzene solution, giving a beautiful wine-red coloration.[3]

Experimental

I. Five grams of monobromocholestanone is dissolved in 50 cc. of dimethylaniline and heated for eight hours so that the solution boils gently. The reaction mixture is poured into iced hydrochloric acid and the half solid precipitate taken up with ether. The ether solution is washed thoroughly with hydrochloric acid, water, soda solution and again water, dried and evaporated. A brown oil which partly crystallizes is obtained. By dissolving in acetone and chilling crystals are obtained which, by several recrystallizations, become white. They melt at 125–126°. With phenylhydrazine the tetrahydrocarbazol derivative described by Doré and Petrow[4] is obtained, melting point 167–182°. The mixed melting point with the tetrahydrocarbazol derivative m. p. 165.5–181° (Doré and Petrow 180–181°) prepared from pure cholestanone was found to be 168–182.5°. From the tetrahydrocarbazol derivative the picrate was prepared which melted at 208–209.5° (Doré and Petrow 209–210°).

II. Five grams of dibromocholestanone is heated with 50 cc. of pyridine. After a short time (twenty to thirty minutes) the precipitation of white crystals begins and soon the flask is filled with them, so that the mixture starts to bump. It is now cooled, filtered and the crystals washed with alcohol. After one recrystallization from alcohol, in which they are difficultly soluble, white shining needles are obtained which show decomposition above 280°, but no melting point. By pouring alkali on the crystals, they take up a beautiful orange coloration, characteristic of pyridinium compounds. Analysis showed them to contain bromine and nitrogen: calcd. for $C_{32}H_{49}ONBr$: N, 2.58; Br, 14.76. Found: N, 2.49; Br, 14.98.

III. Five grams of dibromocholestanone is heated with 50 cc. of dimethylaniline for five hours. The reaction mixture is treated as in Expt. I. After evaporation of the ether, a dark-brown colored oil remains to which was added a small amount of alcohol. By standing for several days in the ice-box, a small amount of crystals came out, the main part being a brown oil. As it was too difficult to separate the crystals, the mixture was taken up with ethyl acetate and alcohol added. Light brown flakes precipitated which were filtered and recrystallized four times from ethyl acetate and alcohol, finally from ethyl acetate: 50 mg. of white needles was obtained, melting point 230–232°.

Calcd. for $C_{33}H_{47}N$: C, 86.65; H, 10.27; N, 3.08. $C_{34}H_{49}N$: C, 86.63; H, 10.40; N, 2.97. $C_{35}H_{53}N$: C, 86.24; H, 10.87; N, 2.87. Found: C, 86.63; H, 10.37; N, 3.13.

A small amount of the substance was dissolved in alcohol and several drops of acetic acid added. After further addition of a solution of *p*-nitrodiazobenzene a deep wine-red coloration was obtained.

(3) We have also carried out experiments in which potassium acetate was used for the removal of the bromine. These experiments were made in acetic acid, ethyl alcohol, butyl alcohol and dioxane as solvents. Our results agree only partly with Butenandt *et al.*[1e] so that further investigation of these reactions seems necessary. Potassium phenolate gave a substance which coupled with *p*-nitrodiazobenzene in alkaline solution to give a deep bluish-red. This substance may also be a derivative of a diphenyl-like combination of the phenol with the cholestanone.

(4) Doré and Petrow, *J. Chem. Soc.*, 1392 (1935).

RESEARCH LABORATORY
SCHERING CORPORATION
BLOOMFIELD, N. J.

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Synthesis of *d,l*-Alanine in Improved Yield from α-Bromopropionic Acid and Aqueous Ammonia

BY WALTER C. TOBIE AND GILBERT B. AYRES

After having synthesized *d,l*-alanine by the excellent but tedious method of Kendall and McKenzie,[1] we decided to try to adapt the method of Orten and Hill[2] for glycine to making *d,l*-alanine from α-bromopropionic acid and aqueous ammonia.

The following method has been worked out and is giving satisfactory results. Pour slowly and with stirring, 100 g. (0.65 mole) of cold (1–4°) α-bromopropionic acid (Eastman No. 981) into 3 liters (44.5 moles) of cold (1–4°) concentrated aqueous ammonia (sp. gr. 0.90) in a glass-stoppered bottle. Allow the mixture to stand at room temperature (below 40°) for at least four days. Evaporate under reduced pressure on a steam-bath to about 300 cc. Filter and evaporate to about 200 cc., cool, add 1 liter of methanol and cool overnight at 1–4°. Filter off the crystals of *d,l*-alanine and wash with methanol and ether; yield 42–46 g., 72–79% of theoretical. Recrystallize the crude product by dissolving in 200 cc. of hot water and by adding 1 liter of methanol, cooling and washing as before; yield 38–40 g., 65–68% of theoretical. This product is bromide free and contains only small amounts of ammonia which may be removed by using Permutit on the second crystallization or recrystallizing a third time. The purified product has a melting point of 194–195° dec., and contains 15.79% nitrogen (same as theoretical).

Other syntheses were carried out in the cold (1–4°) but this did not affect the yield. A temperature above 40° reduced the yield. A reaction time of less than four days cut down the yield, whereas a time of more than four days did not increase the yield. α-Chloropropionic acid gave poorer yields (43–46% of the theoretical) than the α-bromo acid.

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DEPARTMENT OF BIOLOGY AND PUBLIC HEALTH
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.

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(1) Kendall and McKenzie, *Org. Syntheses*, **9**, 4 (1929).

(2) Orten and Hill, THIS JOURNAL, **53**, 2797 (1931).