(m. p. 184°-184.5°); difficultly soluble in cold water, moderately in boiling; quite soluble in cold alcohol, easily in boiling.

(5) *2-Isopropyl-4-Ketodihydroquinazoline.*—About 2 grams of the isobutyrylanthranilic nitrile, 25 cc. hydrogen dioxide solution, and 25 cc. 10 per cent. potassium hydroxide solution, were warmed together at 50°, all gradually dissolving. The solution was precipitated by hydrochloric acid, the precipitate not readily dissolving in an excess of the precipitant, and excess of strong ammonia water was then added. The bulky white precipitate which was thrown down, when recrystallized from dilute alcohol, appeared as long, colorless, silky hairs (m. p. 233°), readily identified as the 2-isopropyl-4-ketodihydroquinazoline.

The *picrate* crystallized from alcohol in yellow prisms (m. p. 208°-208.5°), at which point they turned brown and appeared to decompose. They began to darken at 205°.

(6) *2-Isobutyl-4-Ketodihydroquinazoline.*—This substance was prepared from the isovalerylanthranilic nitrile in the manner just outlined. The bulky white precipitate thrown down by ammonia water was recrystallized from dilute alcohol, giving crystals of the quinazoline, melting at 194.5°-195.5°.

The melting-point of the *picrate* was found to be 188°-189°.

In general, the yield of quinazoline obtained by the use of warm, alkaline hydrogen dioxide solution was much better than that resulting from heating the acylanthranilic nitriles in sealed tubes with anhydrides.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, June, 1902.

THE ACTION OF ISO-VALERIC ALDEHYDE UPON ANTIPYRINE.[1]

BY DAVID C. ECCLES.

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THE investigations of Knorr[2] and Schuftan[3] show that antipyrine is capable of forming condensation products with both aliphatic and aromatic aldehydes. Knorr, by treating a slightly

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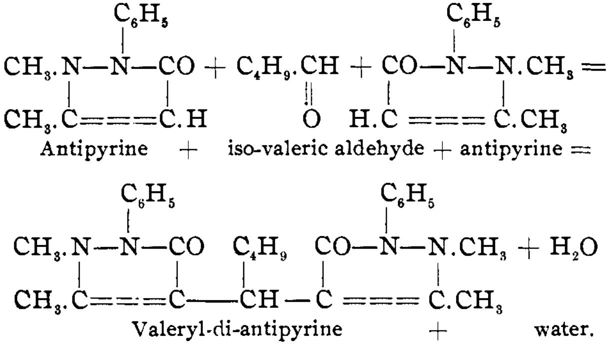
[1] The work here reported was done in Havemeyer Hall, Columbia University, under the direction of Prof. M. T. Bogert.

[2] *Ann. Chem.* (Liebig), **238**, 214.

[3] *Ber. d. chem. Ges.*, **1**, 1181, 1189 (1895).

acid, concentrated aqueous solution of antipyrine with benzaldehyde and neutralizing, procured benzylidene-di-antipyrine. Schuftan, at a later date, by using formaldehyde instead of benzaldehyde, produced the corresponding methylene-di-antipyrine. As these condensations take place readily and give good yields of product it was concluded that 1 molecule of iso-valeric aldehyde might also combine with 2 molecules of antipyrine to give valeryl-di-antipyrine, according to this reaction:



$$\begin{array}{lllll}
 & C_6H_5 & & & C_6H_5 \\
 & | & & & | \\
CH_3.N- & N-CO & + C_4H_9.CH + & CO- & N-N.CH_3 = \\
| & | & \quad\;\; \| & | & \quad\; | \\
CH_3.C= & ==C.H & \quad\;\; O & H.C = & ==C.CH_3
\end{array}$$

Antipyrine + iso-valeric aldehyde + antipyrine =

$$\begin{array}{lllll}
 & C_6H_5 & & & C_6H_5 \\
 & | & & & | \\
CH_3.N- & N-CO & C_4H_9 & CO- & N-N.CH_3 + H_2O \\
| & | & | & | & | \\
CH_3.C= & ==C- & -CH- & C = & ==C.CH_3
\end{array}$$

Valeryl-di-antipyrine + water.

On trial this was found to be the case. The aldehyde and base, mixed in the proportion of 1 molecule of iso-valeric aldehyde and 2 molecules of antipyrine, along with enough hydrochloric acid to give a faintly acid reaction, were heated in a flask connected with a return condenser, for six hours, at 100° C., and then allowed to cool. The resulting oily liquid was poured into a small amount of concentrated potassium hydroxide solution, at once diluted with water and then stirred vigorously. After several hours' standing, an oily layer which separated changed into a white solid. This being filtered off was washed with cold water and then thoroughly dried. On crystallizing it from ligroin its melting-point was found to be 160°-161° C. The yield was about 40 per cent. of the amount calculated from the reaction cited.

The condensation here described was repeated several times and on each occasion the resulting product was composed of fine, white crystals, insoluble in cold water, slightly soluble in hot water and very soluble in alcohol. It was freely soluble in all dilutions of alcohol with water up to two of the latter to one of the former. Hot naphtha and ligroin readily dissolved it. With hydrochloric acid this new derivative combined to form a hydrochloride and with sulphuric acid to form a sulphate. The hydrochloride was prepared by covering the condensation product with water and adding concentrated hydrochloric acid by drops. The solid slowly went into solution but, after a few minutes' standing, separated again as long, feathery needles. These were quite soluble in water and still more readily in the presence of a slight amount of hydrochloric acid. The sulphate was prepared in a similar manner from sulphuric acid but it was much less soluble and therefore separated more readily and completely.

With ferric chloride the hydrochloride gave a thick, reddish brown precipitate which dried to a brownish powder. This was soluble in alcohol and possessed a sharp astringent taste quite unlike the almost tasteless free valeryl base. This ferric derivative is analogous to ferripyrine—the ferric chloride compound of antipyrine. With Mayer's reagent both the hydrochloride and sulphate gave a white, curdy precipitate. When valeryl-di-antipyrine is warmed with concentrated sulphuric acid and sugar it gives a distinct odor like that of valerianic acid.

A determination of the nitrogen contained in valeryl-di-antipyrine gave 13 per cent. nitrogen. Calculated for $C_{27}H_{32}O_2N_4$, the nitrogen would be 12.3.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEBRASKA WESLEYAN UNIVERSITY.]

ON THE REDUCTION OF SOME AROMATIC NITRO-COMPOUNDS.

BY F. J. ALWAY AND M. D. WELSH.

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IN THE following paper we give the results thus far obtained from a study of the reduction of *p*-nitrobenzaldehyde and *m*-nitrobenzaldehyde in neutral solution. As this work is for a few months necessarily interrupted and as we will be unable to continue it together we consider it best to publish the results already at hand. The investigation was undertaken in the hope that we might be able to isolate from the reduction products of the nitro-