123. *Strychnine and Brucine. Part XXIX.* N(b)-*Methyldihydro*chano*pseudostrychnine.*

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In Part XX (J., 1932, 2305) the present authors described *N*(*b*)-methyl*chano*pseudostrychnine and noted that it yielded a dibenzylidene derivative. One of these benzylidene residues was considered to be in the usual benzylidenestrychnine position, that is, in a group $\colon N(a)\cdot CO\cdot\dot{C}\colon CHPh$; the other was diagnostic of a $-CO-CH_2-$ or $-CO\cdot\dot{C}=\dot{C}-CH_2-$ structure.

We have now obtained N(b)-*methyldihydro*chano*pseudostrychnine* by reduction of methyl*chano*pseudostrychnine in dilute acetic acid solution by means of hydrogen in the presence of platinum-black. This characteristic base furnishes a *benzylidene* derivative and, although there was evidence of further condensation, no crystalline dibenzylidene derivative could be isolated.

The result is not quite conclusive, but it favours the view that the second reactive methylene in *N*(*b*)-methyl*chano*pseudostrychnine is included in a system $\cdot CO\cdot\dot{C}=\dot{C}-CH_2-$. It would, then, follow that *N*(*b*)-methyl*chano*pseudostrychnine is a derivative of *neo*strychnine, the movement of the double link occurring in the course of the hydrolysis of des-*NO*-dimethylpseudostrychninium hydroxide as already suggested.

In a recent memoir (*Ber.*, 1934, **67**, 108) Leuchs and Beyer have described an isomeride of benzylidenedihydrostrychnine which is remarkable on account of its failure to exhibit the Otto strychnine reaction. It is therefore of interest to recall that the present authors (Part XX, *loc. cit.*) obtained a compound, m. p. 153°, by condensation of des-*NO*-dimethylpseudostrychninium hydroxide with benzaldehyde and that this substance, also, exhibited no Otto reaction. It is highly probable that the same phenomenon is concerned in both cases. Leuchs and Beyer put forward the suggestion that the aromatic nucleus of the benzaldehyde is attacked by the carbonyl of $\colon N(a)\cdot CO\cdot$ with formation of a hydrindene derivative. This type of reaction is, however, very unusual and we suggest as alternative explanations (1) that a rearrangement has occurred and that a true aromatic indole nucleus has been formed, (2) that $\colon N(a)\cdot CO-$ has become a unit in a pyridone structure, or (3) that the benzaldehyde has attacked the *p*-position in the aromatic nucleus.

Experimental.

Catalytic Reduction of N(b)-*Methyl*chano*pseudostrychnine.*—A solution of the base (2 g.) in 10% acetic acid (40 c.c.) was shaken with platinum-black (0·2 g.) in an atmosphere of hydrogen, which was rapidly absorbed until, after about 2 hours, rather more than 1 mol. had been taken up. After shaking for a further 30 minutes the catalyst was filtered off, and the reduced base precipitated in a crystalline condition by the addition of aqueous ammonia to the boiling filtrate. N-*Methyldihydro*chano*pseudostrychnine* crystallises from alcohol, in which it is sparingly soluble, in large, thin, colourless prisms, m. p. 296—297° (Found : C, 72·2, 72·2; H, 7·1, 7·5; N, 7·9. $C_{22}H_{26}O_3N_2$ requires C, 72·1; H, 7·1; N, 7·7%).

The same substance was obtained when palladised barium sulphate was used as catalyst, but in this case the reduction proceeded considerably more slowly. Whereas the unreduced base gives a sparingly soluble and highly crystalline perchlorate, the perchlorate of the reduced compound could not be crystallised, and is considerably more soluble.

Benzylidene-N(b)-*methyldihydro*chano*pseudostrychnine*.—The reduced base (0·5 g.), finely powdered, was boiled with benzaldehyde (0·75 c.c.) and aqueous potassium hydroxide (2 drops of 40%) in alcohol (5 c.c.). It dissolved rapidly, and after 3 minutes the clear solution was poured into 0·5*N*-hydrochloric acid (100 c.c.). The yellow solution was washed with ether to remove benzaldehyde, heated to boiling, and neutralised with ammonia. After cooling, the amorphous product was collected, and stirred with alcohol; a red gum was extracted and the residue crystallised. It was twice crystallised from alcohol, giving the *benzylidene* derivative in rosettes of small, pale yellow needles, m. p. 264—266° (Found: C, 74·2; H, 6·7; N, 6·0. $C_{29}H_{30}O_3N_2,H_2O$ requires C, 73·7; H, 6·8; N, 5·9%). Partial dehydration to the extent of 17% of $1H_2O$ is required in order to bring the analytical figures into exact agreement with theory. The substance dissolves in sulphuric acid with a yellow colour, and it gives the blue Otto reaction characteristic of benzylidenestrychnine. Longer heating of the reactants favoured an increased formation of the red gum at the expense of the crystalline material.

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