ent International value for the atomic weight of sodium is 0.003–0.004 unit too high.

DEPARTMENT OF CHEMISTRY
THE RICE INSTITUTE
HOUSTON, TEXAS
ARTHUR F. SCOTT
FRANK H. HURLEY, JR.

RECEIVED JUNE 4, 1937

SYNTHETICAL EXPERIMENTS IN THE CHELIDONINE-SANGUINARINE GROUP OF ALKALOIDS

Sir:

In a recent article under the above title that has just come to our attention, Richardson, Robinson and Seijo [*J. Chem. Soc.*, 835 (1937)] report a general scheme for the synthesis of bases of the chelerythrine-sanguinarine type. We have been working in this field for the past two years and certain of our experiments have paralleled those reported by Robinson and his co-workers. While our work has not progressed as far as that of Professor Robinson, we should like to continue our efforts in this field and to submit a brief outline of what we have been doing.

Attempts to apply the Pschorr phenanthrene synthesis in the synthesis of phenanthridines were no more successful than those of the above authors. Instead of using 6-nitropiperonal in our trial experiments we used *o*-nitrobenzaldehyde which condensed readily with α-naphthylamine. The Schiff base was reduced with tin and hydrochloric acid to give two products, one of which formed a monohydrochloride and the other a dihydrochloride. Both compounds gave diazonium salts as indicated by coupling with β-naphthol but treatment with copper powder under various conditions gave only tar. Since it is possible that a *trans* configuration of the Schiff base prevents ring closure, the nitro compound was converted to the methochloride, reduced with tin and hydrochloric acid and diazotized, but again treatment with copper powder gave only tar.

Thinking that ring closure in the β-position of the naphthalene nucleus might be difficult, attempts were made to bring about closure from the naphthalene side. Benzaldehyde could not be made to condense with *o*-nitroaniline so no attempt was made to condense it with 2-nitro-α-naphthylamine. On the other hand, piperonylmethylamine condensed with *o*-nitrochlorobenzene. Treatment of the reduced and diazotized compound with copper powder did not give as much tar as previously but none of the desired phenanthridine has yet been isolated.

We also have been attempting to apply the phenylnaphthylenediamine synthesis of Atkinson and Thorpe to the synthesis of benzophenanthridines, our starting material for trial runs being benzyl cyanide. In view, however, of the inability of Robinson and Liguori to bring about ring closure in the piperonyl and veratryl series, we shall probably discontinue our own efforts in this direction.

Our first work in this field was an attempt to apply a modification of the Bischler–Napieralski synthesis of isoquinolines. The N-piperonylamides of γ-piperonylisocrotonic acid and γ-piperonylpropionic acid were prepared but all attempts at ring closure were unsuccessful. Apparently ring closure can be effected only when the nitrogen atom becomes a part of the ring which is formed.

Work on a series of reactions almost identical with those successfully used by Robinson and co-workers has been barely started. It differs in that we have been attempting to synthesize α,γ-dipiperonylbutyric acid through piperonylmalonic ester and piperonylmethyl bromide and we expect to continue with this phase of the synthesis.

It will be noted from the formulas of Bruchhausen and Bersch [*Ber.*, **63**, 2520 (1930)] that orthoveratraldehyde and orthopiperonal will be needed for the syntheses of the alkaloids themselves. We should therefore like to report the successful methylenation, using methylene sulfate, of 2,3-dihydroxybenzaldehyde obtained from the commercially available orthovanillin, a series of reactions that is much simpler than that reported by Perkin and Trikojus [*J. Chem. Soc.*, 2925 (1926)].

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIV., CALIF.
C. R. NOLLER
R. O. DENYES
J. W. GATES
W. L. WASLEY

RECEIVED SEPTEMBER 23, 1937