

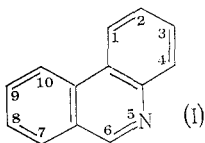
## PHENANTHRIDINES

### VI.\* THE BROMINATION OF PHENANTHRIDINE

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It is now possible to correlate the positions of electrophilic substitution in a number of heterocyclic compounds with the reactivity of positions predicted by one or other of the theoretical reactivity parameters.<sup>1</sup> Phenanthridine, because of its nine non-equivalent positions for attack, offers a sterner test of the ability of theoretical calculations to predict the most likely positions of attack in electrophilic substitution.



It is interesting to note that Eisch and Gilman<sup>2</sup> found that bromination of phenanthridine (I) gave only 2-bromophenanthridine when effected with *N*-bromosuccinimide. Nitration<sup>3</sup> has been shown to give 1-, 2-, 3-, 4-, 8-, and 10-nitrophenanthridines.

In the present work phenanthridine was brominated by the method of Derbyshire and Waters,<sup>4</sup> which gives rise to positive bromine. Bromine (0.8 mole) was added to a solution of phenanthridine and silver sulphate in 92% sulphuric acid. The crude mixture of products was separated into seven fractions by chromatography on alumina. These fractions were further separated by chromatography on silica gel or by using  $pK_a$  differences in the products. The quantities of each compound isolated (from 5.000 g phenanthridine) are as follows: dibromophenanthridines, 0.137 g; 10-bromo, 0.456 g; 4-bromo, 0.308 g; 2-bromo, 0.048 g; phenanthridine, 1.445 g; unidentified material, 0.182 g. Thus 2-bromophenanthridine, 4-bromophenanthridine, and 10-bromophenanthridine were isolated in the following order of abundance:  $10 > 4 \gg 2$ , while a large proportion of unchanged phenanthridine was recovered. Small quantities of dibromophenanthridines were shown to be produced. The identities of the bromination products were established by comparison of melting points and infrared spectra with those of authentic samples.<sup>5</sup>

While the limitations of this qualitative investigation are realized, nevertheless it suggests that the reactivity of the positions in phenanthridine towards electrophilic

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<sup>1</sup> Ridd, J., in "Physical Methods in Heterocyclic Chemistry." (Ed. A. Katritzky.) (Academic Press: New York 1963.)

<sup>2</sup> Eisch, J. J., and Gilman, H., *J. Am. chem. Soc.*, 1955, **77**, 6379.

<sup>3</sup> Caldwell, A. C., and Walls, L. P., *J. chem. Soc.*, 1934, 104.

<sup>4</sup> Derbyshire, D. H., and Waters, W. A., *J. chem. Soc.*, 1950, 564, 573.

<sup>5</sup> Badger, G. M., and Sasse, W. H. F., *J. chem. Soc.*, 1957, 4; Huppatz, J. L., and Sasse, W. H. F., *Aust. J. Chem.*, 1964, **17**, 1406; 1965, **18**, 206; Chandler, G. S., Huppatz, J. L., Jones, R. A., and Sasse, W. H. F., *Aust. J. Chem.*, 1967, **20**, 2037.

bromination under these conditions is  $10 > 4 > 2$ . This contrasts with the order observed in nitration which is  $1 > 10 > 8 > 3 > 2 > 4$ . The nitrations show some agreement with localization energy calculations for the cation, which predict the following order of reactivities:<sup>6</sup>  $10 > 1 > 8 > 3 > 4 > 2 > 7 > 9$ . The present brominations are better anticipated by the order which would be expected from the electron density calculations made by Longuet-Higgins and Coulson<sup>7</sup> for the neutral molecule, which indicate that the reactivities in electrophilic substitution should be  $4 > 10 > 8 \simeq 2$ .

### Experimental

Microanalyses were performed by the Australian Microanalytical Service, Melbourne. Thin-layer chromatography (t.l.c.) of the phenanthridines was carried out using silica gel with benzene-ether (4 : 1) as eluent.

Silver sulphate (8.0 g) was added to a solution of phenanthridine (10.0 g; 0.056 mole) in 92% sulphuric acid (50 ml) and bromine (2.3 ml; 7.18 g; 0.045 mole) was added when all the sulphate had dissolved. The mixture was shaken in a closed vessel for  $5.5 \text{ hr}$  at  $23 \pm 0.5^\circ$ . The reaction mixture was filtered and the residue was washed with concentrated sulphuric acid ( $2 \times 20 \text{ ml}$ ) and hot water ( $2 \times 20 \text{ ml}$ ). The acidic filtrate was diluted with water, basified with aqueous ammonia, and extracted with ether. An ether-insoluble black tar (1.2 g) was removed. Removal of the solvent from the dried ethereal solution left a brown solid (10.03 g). The solid (5 g) was chromatographed on alumina to give seven fractions, A (0.09 g), B (0.258 g), C (0.313 g), D (1.68 g), E (1.92 g), F (0.074 g), and G (0.253 g). A was crystallized from light petroleum, b.p.  $60\text{--}80^\circ$ , and then ethanol-water to give colourless needles of a dibromo derivative, m.p.  $143.5\text{--}144.5^\circ$  (Found: C, 45.7; H, 2.0; N, 3.9. Calc. for  $\text{C}_{13}\text{H}_7\text{Br}_2\text{N}$ : C, 46.3; H, 2.1; N, 4.2%). B was homogeneous on t.l.c. ( $R_F$  0.81;  $R_F$  of 4-bromophenanthridine 0.79) and on crystallization from light petroleum gave colourless plates, m.p.  $129\text{--}130.5^\circ$ , alone or mixed with 4-bromophenanthridine. The mixture F was not further examined. G crystallized from light petroleum to give phenanthridine, m.p.  $105\text{--}106^\circ$  alone and mixed with an authentic sample.

The fractions C and D were rechromatographed on silicic acid. C gave rise to 4 fractions, H (0.050 g), I (0.047 g), J (0.080 g), and K (0.148 g). H was 4-bromophenanthridine, identified as before. Fraction I was crystallized from light petroleum to give colourless plates of a dibromo derivative, m.p.  $148\text{--}151^\circ$  (Found: C, 47.1; H, 2.4. Calc. for  $\text{C}_{13}\text{H}_7\text{Br}_2\text{N}$ : C, 46.3; N, 2.1%). Thin-layer chromatography of J gave two spots,  $R_F$  0.45 (2-bromophenanthridine  $R_F$  0.48 and 9-bromophenanthridine  $R_F$  0.42) and  $R_F$  0.67 ( $R_F$  3-bromophenanthridine 0.66), which was not further examined. K was identified by mixed melting point to be phenanthridine.

Chromatography of D gave two fractions (0.015 g and 0.013 g) which were not further examined, together with 10-bromophenanthridine (0.056 g) and phenanthridine (1.0 g).

The eluate E, after crystallizing from light petroleum, was dissolved in 0.5N sulphuric acid and the solution was gradually basified giving three crystalline precipitates, W (0.643 g), X (0.20 g), and Y (0.08 g). W, after two crystallizations from light petroleum, gave 10-bromophenanthridine (0.40 g), identical in infrared spectrum with an authentic specimen. X crystallized from light petroleum to give 2-bromophenanthridine (0.048 g), m.p.  $161.5\text{--}162.5^\circ$ ; its infrared spectrum was identical with that of authentic 2-bromophenanthridine. Phenanthridine (0.052 g), m.p.  $105\text{--}106^\circ$ , was obtained by crystallizing Y once from light petroleum.

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<sup>7</sup> Longuet-Higgins, H. C., and Coulson, C. A., *Trans. Faraday Soc.*, 1947, 43, 87.