acetone. The solid was dried in a high air velocity hood and finely ground.

X-Ray diffraction patterns were recorded both on a North American Philips High Angle Spectrometer and with a 114.59-mm. diameter powder camera using Ni filtered Cu radiation (λ 1.5418 Å.). The 29 lines obtained and the planes to which they are attributed are listed in Table I. The tetragonal unit cell constants derived from the patterns are listed in Table II. Using these constants, d values were calculated which agreed with the observed values to better than 1%. The density of the pigment was determined by water displacement in a 25-ml. pycnometer.

TABLE I

THE X-RAY DIFFRACTION PATTERN OF α-$C_{32}H_{16}N_8Cu$

(hkl)	d, Å.	I/I_0	(hkl)	d, Å.	I/I_0
001	12.790	1.0	610	2.836	0.3
110	12.190	0.9	620	2.722	.2
200	8.630	.4	005	2.532	.2
201	7.196	.1	613	2.365	.1
002	6.417	.1	524	2.254	.1
310	5.490	.7	444	2.229	.2
320	4.796	.1	006	2.118	.5
400	4.353	.1	661	2.037	.1
330	4.068	.1	900	1.935	.2
411	3.678	.7	007	1.848	.1
500	3.486	.7	770	1.757	.4
510	3.395	.9	904	1.651	.2
520	3.226	.9	881	1.523	.1
342	3.100	.2	009	1.421	.1
333	2.931	.2			

TABLE II

UNIT CELL CONSTANTS OF α-$C_{32}H_{16}N_8Cu$

a_0 = 17.367 Å.
c_0 = 12.790 Å.
Z = 6 ($C_{32}H_{16}N_8Cu$)
$d_{\text{calcd.}}$ = 1.488 g./cm.^{3}
$d_{\text{meas'd.}}$ = 1.49 g./cm.^{3}
Probable space group C^1_{4h} – P4/m

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A New Synthesis of Phenanthridine[1]

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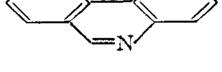
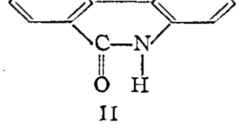
RECEIVED AUGUST 11, 1952

Phenanthridine (I) has been prepared from phenanthridone (II) by distillation with zinc dust,[2] by reduction with lithium aluminum hydride in 70% yield,[3] and by conversion to 9-bromophenanthridine in unspecified yield[4] followed by dehalogenation with hydrogen and Raney nickel.[5] The first method is of theoretical rather than practical interest; the second is not suitable for the preparation of large quantities of phenanthridine, and the amount of lithium aluminum hydride must be carefully controlled to avoid formation of 9,10-dihydrophenanthridine[6]; and the third requires phosphorus oxybromide, which is not readily available. Attempts to prepare phenanthridine by dehalogenation of the more readily prepared 9-chlorophenanthridine gave 9,10-dihydrophenanthridine.[6] It has been stated recently that "there seems to be no really satisfactory method for the conversion of phenanthridone into phenanthridine on a large scale."[6]

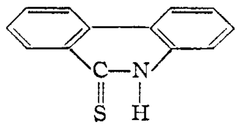


I



II

Phenanthridine has now been prepared from phenanthridone in 89.5% over-all yield by conversion to the previously unknown phenanthridinethione (III) followed by desulfurization with Raney nickel in dimethylformamide–ethanol solution. This method is suitable for large scale preparations, and the phenanthridine thus obtained is free of the 9,10-dihydro derivative.



III

Experimental[7]

Phenanthridinethione.—A mixture of 20 g. of phenanthridone, 30 g. of phosphorus pentasulfide and 300 ml. of pyridine was heated under reflux for two hours. The reaction mixture was then poured into one liter of water, and the precipitated yellow solid was separated by filtration, washed thoroughly with water and recrystallized from aqueous dimethylformamide. The phenanthridinethione (20.3 g., 94%) was obtained in the form of long, yellow needles, m.p. 281–283°. The analytical sample was prepared by sublimation at 200° (1 mm.).

Anal. Calcd. for $C_{13}H_9NS$: C, 73.9; H, 4.3; N, 6.6. Found: C, 74.2; H, 4.5; N, 6.5.

Phenanthridine.—A mixture of 30 g. of phenanthridinethione, 120 g. (weighed wet with water) of Raney nickel catalyst,[8] 300 ml. of dimethylformamide and 300 ml. of ethanol was heated under reflux for one hour. The colorless solution, exhibiting a strong blue fluorescence, was filtered, and the filtrate acidified with hydrochloric acid and evaporated to dryness under reduced pressure. The residue was dissolved in 100 ml. of water, the solution treated with Norit and the filtrate made alkaline with aqueous ammonium hydroxide. Upon standing, phenanthridine (24.1 g., 95%) separated as a white crystalline mass; m.p. 99–100°. One recrystallization from aqueous acetone gave colorless plates of pure phenanthridine, m.p. 106°.

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(1) For recent reviews on phenanthridine syntheses, see (a) L. P. Walls in "Heterocyclic Compounds," Vol. IV, edited by R. C. Elderfield, John Wiley and Sons, Inc., New York, N. Y., 1952, p. 564; (b) R. S. Theobald and K. Schofield, *Chem. Revs.*, **46**, 171 (1950); (c) E. A. Braude and J. S. Fawcett, *J. Chem. Soc.*, 3113 (1951).

(2) A. Pictet and H. J. Ankersmit, *Ann.*, **266**, 138 (1891).

(3) P. de Mayo and W. Rigby, *Nature*, **166**, 1075 (1950).

(4) L. P. Walls, *J. Chem. Soc.*, 104 (1934).

(5) A. Albert, D. J. Brown and H. Duewell, *ibid.*, 1284 (1948).

(6) G. M. Badger, J. H. Seidler and B. Thompson, *ibid.*, 3207 (1951).

(7) All melting points are corrected. Microanalyses were carried out by Mrs. Katherine Pih, Mrs. Esther Fett and Mr. Joseph Nemeth.

(8) A commercially available grade of Raney nickel catalyst in water (Raney Catalyst Co., Chattanooga, Tennessee) was employed. Less catalyst was necessary and a shorter reaction time was possible when fresh Raney nickel (D. J. Brown, *J. Soc. Chem. Ind.*, **69**, 353 (1950)) was employed.