4,6-O-Benzylidene-1-deoxy-1-(d-α-methylphenethylamino)-D-fructose oxalate (IIc). A solution of compound Ic in 150 ml. of methanol was prepared, as described above, from 20.7 g. of *d*-α-methylphenethylamine and 41.4 g. of 4,6-*O*-benzylidene-D-glucose. To this filtered solution was added, in one portion at room temperature, a filtered solution of 18.7 g. of oxalic acid dihydrate in 100 ml. of methanol. After standing overnight at room temperature, the reaction mixture was concentrated almost to dryness, and the crystalline product (68 g., m.p. 123–129° with decomposition) was collected at the filter. Recrystallization from 170 ml. of 95% ethanol gave 26 g., m.p. 126–130°. Two more recrystallizations of a sample gave pure IIc, m.p. 130–131°.

Anal. Calcd. for $C_{22}H_{27}NO_5.(COOH)_2$: C, 60.62; H, 6.15. Found: C, 60.47; H, 6.35. $[\alpha]^{26}_{D}$ −26.4° (c 1.110 in H_2O).

This product rapidly reduces methylene blue in alkaline solution.

Acknowledgment. The author is indebted to Mr. E. F. Shelberg and Mr. William Washburn and their associates for the microanalyses and infrared spectra, respectively, and to Mr. Nick Ryan for technical assistance.

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5-Amino-3-chloropyridazine. A Clarification

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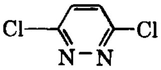
Recently Steck[1] reported that the treatment of 3,6-dichloropyridazine (I) with sodium amide yielded a product whose structure was suggested to be 5-amino-3-chloropyridazine (II). This structure was based on a melting point depression on admixture with authentic 3-amino-6-chloropyridazine (III).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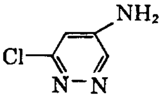
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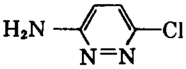
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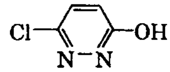
IV

Such a rearrangement appeared somewhat surprising in view of the high reactivity of a chlorine atom of 3,6-dichloropyridazine to direct displacement.[2] A similar rearrangement, involving 3-bromopyridine, has been reported by Levine and Leake[3]; however, this involved a relatively inert halogen atom.

Our attempts to repeat Steck's experiment resulted in the isolation of 3-chloro-6-hydroxypyridazine (IV) in low yield, together with a 50% recovery of the starting material, 3,6-dichloropyridazine. A direct comparison of the presumed 5-amino-3-chloropyridazine[4] with authentic 3-chloro-6-hydroxypyridazine established that they were indeed the same. The latter was prepared by a modification of Steck's method[5] of acid hydrolysis of 3,6-dichloropyridazine. The identity was based on elemental analysis, mixed melting point, and infrared comparisons of the two products.

Evidently in the original experiment the 3,6-dichloropyridazine largely survived the sodium amide treatment. It was then extracted by the hydrochloric acid, and underwent hydrolysis during the process of concentration in the acid medium. The possibility that 3-amino-6-chloropyridazine was formed in more than a minor amount in the attempted amination of 3,6-dichloropyridazine was eliminated, since this amine was shown to be inert to refluxing 6*N* hydrochloric acid.

EXPERIMENTAL[6]

3-Chloro-6-hydroxypyridazine.[5] Five grams (0.034 mole) of 3,6-dichloropyridazine in 300 ml. of 0.6*N* hydrochloric acid was refluxed for 3 hr. After removal of the unchanged 3,6-dichloropyridazine by steam distillation, the reaction mixture was concentrated at reduced pressure and was then chilled. A white, crystalline solid (2.3 g., 53%) was obtained, melting at 141.5–142.0°. Recrystallization from ethyl acetate raised the melting point to 142.0–142.5°.

Anal. Calcd. for $C_4H_3ClN_2O$: C, 36.80; H, 2.32; Cl, 27.17; N, 21.45. Found: C, 36.90; H, 2.54; Cl, 27.82; 27.02, 27.24; N, 21.67, 21.22.

Anal.[7] of the supposed 5-amino-3-chloropyridazine. Found: C, 36.87; H, 2.53; Cl, 27.24; N, 20.98, 21.44, 21.80.

The melting point of this sample was 141.5–142.0° and this was not depressed on admixture with our sample of 3-chloro-6-hydroxypyridazine. Infrared spectra of the two samples were identical; they were obtained in potassium bromide disks on a Perkin-Elmer Infracord Spectrophotometer Model 137.

Attempted hydrolysis of 3-amino-6-chloropyridazine. One gram of 3-amino-6-chloropyridazine in 60 ml. of 6*N* hydrochloric acid was refluxed for 1.5 hr. The cooled solution was adjusted to *p*H 8 and chilled to yield a white precipitate. The dried product (912 mg., 91.2%) melted at 221.5–222.5°; m.p. of starting material, 213.0–214.0°; mixed m.p. 215.0–216.0°. Infrared spectra of the two samples were identical.

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(1) E. A. Steck, *J. Org. Chem.*, **24**, 1597 (1959).

(2) See, among others, J. Druey, K. Meier, and K. Eichenberger, *Helv. Chim. Acta*, **37**, 121 (1954).

(3) R. Levine and W. W. Leake, *Science*, **121**, 780 (1955).

(4) We wish to thank Dr. E. A. Steck of Wilson Laboratories, Chicago 9, Ill., and Dr. G. D. Wessinger of the Sterling-Winthrop Research Institute, Rensselaer, N. Y., for furnishing us with a sample of the compound in question.

(5) E. A. Steck and R. P. Brundage, *J. Am. Chem. Soc.*, **81**, 6511 (1959).

(6) All melting points are corrected.

(7) Performed in our laboratories.