$[\alpha]^{20}_D$ 76.1° (*c* 1.0, water); a mixture melting point was undepressed.

Registry No.—4, 10293-59-1; 7, 17327-17-2.

2-Cyclopropylpyridine

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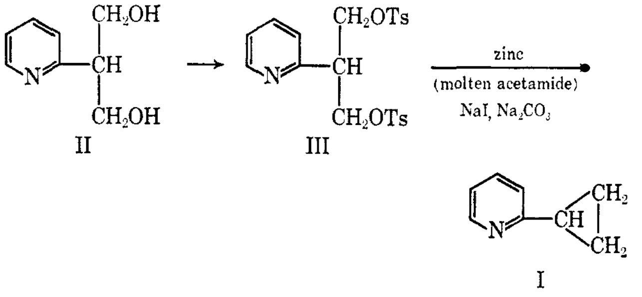
The synthesis of 2-cyclopropylpyridine (I) has previously been reported by one of us.[1] It had been prepared in small quantity in a six-step synthesis. The ultraviolet spectrum had been reported [λ_{max} 2690 Å (log ϵ 3.58)] in absolute alcohol. Although derivatives had been prepared, no analysis had been reported on I itself.[2]

In a recent publication,[3] Gray and Kraus cast doubt as to whether I had been obtained. Although they[3] did not actually prepare I, they did prepare 4-cyclopropylpyridine. Other data[4,5] seem to confirm the earlier report of Gray and Kraus.

It was felt that the unequivocal synthesis of I itself would be necessary to solve the dilemma. A new synthesis of I was achieved and is reported here. Commercially available II[6] was converted into III by standard procedures. Using a modification of the method of Dolbier,[7] III was readily converted into I in 80% yield of crude material. The product, I, was purified by preparative gc and was free from all detectable contamination.



Pure I had a λ_{max} of 2685 Å (log ϵ 3.60) in absolute alcohol. The ir spectrum (neat) and nmr spectrum were consistent with the structure assigned to I; the methinyl proton of the cyclopropyl ring appeared as the expected triplet of triplets at τ 7.8–8.3. A comparison of the spectra of I and cyclopropylbenzene[8] shows the close relation of the two compounds.

From the properties of this product, I, it is clear that the product reported previously was indeed impure. It is not possible to say what percentage of I was in the original product,[1] if indeed there was any, but the uv spectrum of I is essentially identical with that previously reported.

Attempts to prepare I from 2-vinylpyridine and methylene *via* the Simmons–Smith reaction[9] were uniformly unsuccessful.

Experimental Section

All melting points are corrected and were determined on a Fisher-Johns apparatus. Ir spectra were taken on a Beckman IR-4 spectrophotometer. Nmr spectra were taken on a Varian A-60-A instrument. Uv spectra were taken on a Cary 14 spectrophotometer. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Preparation of the Ditosylate of 2-(2-Pyridyl)-1,3-Propanediol (III).—2-(2-Pyridyl)-1,3-propanediol,[6] II (7.65 g, 0.05 mol), was dissolved in dry pyridine (125 ml) and cooled to 0–5°. *p*-Toluenesulfonyl chloride (38 g, 0.02 mol) was slowly added. The mixture was placed in a refrigerator overnight and then poured onto ice–water (700 ml) with stirring. The solid which came out of solution was crystallized from methyl alcohol, giving 15.0 g (65%) of white crystals: mp 106–107°; ir (KBr) 1175 cm^{-1} (tosylate);[10] nmr ($CDCl_3$) τ 1.50–2.67 (m, 12), 5.60 (d, 4), 7.00 (quintet, 1), 7.53 (s, 6).

Anal. Calcd for $C_{22}H_{23}NO_6S_2$: C, 57.23; H, 5.02; N, 3.04. Found: C, 57.22; H, 5.02; N, 3.09.

2-Cyclopropylpyridine (I).—A mixture of dry acetamide (40 g), sodium iodide (1 g), and sodium carbonate (3 g) was heated to 150° in a three-neck flask fitted with magnetic stirrer, thermometer, solid addition device,[11] and a Liebig condenser connected by tubing to a solution of calcium hydroxide. Powdered zinc (AR grade) (8 g, 0.06 mol) was added and the temperature was maintained at 150°. The ditosylate II (9.24 g, 0.02 mol) was slowly added (10 min) through the solid addition flask. Carbon dioxide, as expected, was evolved and formed calcium carbonate in the calcium hydroxide trap.[12] After 10 min, the condenser was removed and the apparatus was set up for distillation. The pot temperature was raised to 220° and a liquid began to distil at a head temperature of 150–180°. No cold water was used in the distilling condenser since acetamide (bp 222°, mp 82°) was distilling over with the product. The distillation was continued for 40 min. Water (50 ml) was added to the distillate, followed by ether (50 ml). The layers were separated and the ether layer was washed with water (three 25-ml portions), dried ($MgSO_4$), concentrated, and distilled, giving 2.0 g (83%) of crude 2-cyclopropylpyridine. The crude liquid was then purified by preparative gc on a dinonylphthalate column. The preparative gc gave a clear, colorless liquid (characteristic alkyl pyridine odor) free from all detectable contamination: bp 184–185° (758 mm), 31° (0.25 mm); n^{25}_D 1.5380; uv λ_{max} (100% ethanol) 268.5 mμ (log ϵ 3.60); ir (neat) 1030 and 1040 cm^{-1}; nmr (CCl_4) τ 2.70 (m, 4), 7.80–8.30 (3 triplets, 1), and 9.15 (m, 4).

Anal. Calcd for C_8H_9N: C, 80.67; H, 7.74; N, 11.76. Found: C, 80.75; H, 7.59; N, 11.69.

The picrate had mp 133–134°.

Anal. Calcd for $C_{14}H_{12}N_4O_7$: C, 48.28; H, 3.47. Found: C, 48.18; H, 3.50).

Registry No.—I, 20797-87-9; I (picrate), 20797-88-0; III, 20797-89-1.

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