NOTES

2, 2'-Binaphthoxazoline

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(Received May 17, 1962)

The reaction between *o*-aminophenol and glyoxal was studied by Bayer[1] and Murase[2]. The condensation product, 2, 2'-bibenzoxazoline, was found to be an organic reagent for various cations and especially selective and specific for calcium. It was used as a metal indicator for calcium in chelatometry[3] and as a colorimetric reagent by extraction[4].

The condensation product of 2-amino-1-naphthol with glyoxal, 2, 2'-binaphthoxazoline, also reacts with calcium to form a deep blue chelate which can be extracted by chloroform;

1) E. Bayer, *Chem. Ber.*, **90**, 2325 (1957).
2) I. Murase, This Bulletin, **32**, 827 (1959); **33**, 59, 607 (1960).
3) D. Goldstein, *Anal. Chim. Acta*, **21**, 339 (1959).
4) K. T. Williams and J. R. Wilson, *Anal. Chem.*, **33**, 244 (1961).

the absorption curve has a maximum at 638 mμ. The chelate is, however, unstable, and the color fades gradually. Therefore, it is usable for the detection but not for the determination of calcium.

Synthesis of 2, 2'-Binaphthoxazoline.—2-Amino-1-naphthol was prepared by the reduction of 2-nitroso-1-naphthol made from α-naphthol. It is very unstable in air, and so its hydrochloride is used for the preparation. Five grams of 2-amino-1-naphthol hydrochloride are dissolved in 1 l. of boiling water containing 10 ml. hydrochloric acid. The solution turns red upon oxidation with air. To reduce the solution, 0.5 g. of tin powder is added and the solution is boiled until it is almost colorless. After cooling quickly, it is filtered. At about 20°C, 3.8 ml. of a 40% glyoxal solution are stirred into it, and then sodium acetate is added until a large volume of a red precipitate is formed (about 20 g. of sodium acetate are needed, and the pH value is 3~4). Three more grams of sodium acetate are added with agitation. The stirring is continued for 1~2 hr. The solution is then allowed to stand for 12 hr., is filtered, and is washed with dilute hydrochloric acid and water. The precipitate is dissolved in 400 ml. of alcohol and decolorized with active carbon. The filtrate is condensed by a rotary evaporator to deposit crystals. They are recrystallized two or three times, affording 100 mg. of pale blue needles which melt at 223°C. The preparation shown above should preferably be done in a dark room, because the compound tends to decompose in daylight.

Found; C, 77.33; H, 4.980; N, 8.280. Calcd. for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23.

The condensation of 1-amino-2-naphthol with glyoxal was not successful.

Detection of Calcium.—One milliliter of the reagent solution (20 mg. in 100 ml. ethanol), 0.4 ml. of an alkaline solution (10 g. sodium hydroxide and 0.5 g. sodium carbonate in 100 ml. water) and 4 ml. of a calcium solution are mixed together in a 15 ml. stoppered tube and then extracted with 5 ml. of chloroform by vigorous shaking. The absorption curve in chloroform (Fig. 1) has a maximum at 638 mμ. The color change and the extractability are very excellent, and so a micro amount of calcium can be detected. However, the color is not very stable and fades gradually. Therefore, the reproducibility is not so good that the quantitative determination cannot be carried out by this method, though the calibration curve can be roughly drawn.

The authors wish to express their deep gratitude to Dr. Ichiro Murase for his kind suggestion in the course of the preparation of 2, 2'-binaphthoxazoline.

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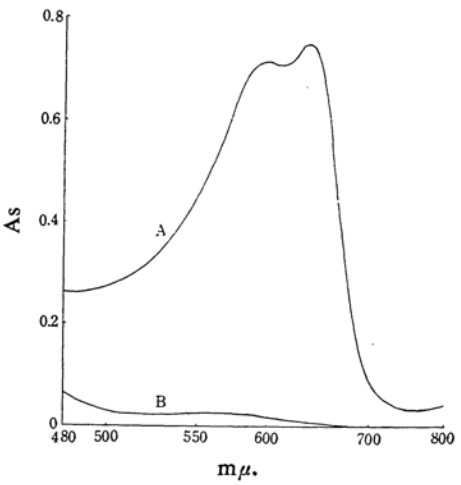

Fig. 1. Absorption curves.
A: 2, 2'-Binaphthoxazoline-Ca complex in chloroform.
B: 2, 2'-Binaphthoxazoline in chloroform (masked a minute amount of Ca in alkaline solution with EDTA).