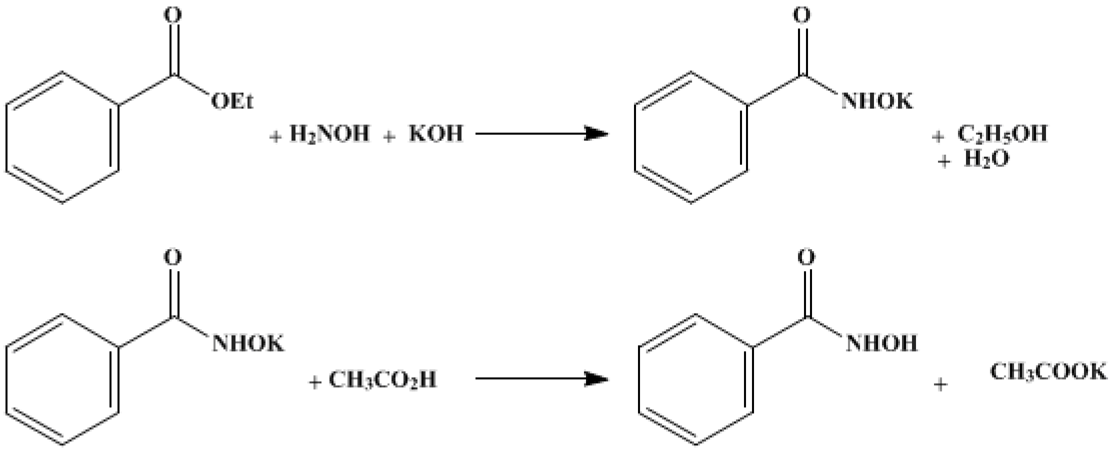
Organic Syntheses, Coll. Vol. 2, p.67 (1943); Vol. 19, p.15 (1939).

BENZOHYDROXAMIC ACID



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1. Procedure

(*A*) *Potassium Benzohydroxamate*.—Separate solutions of 46.7 g. (0.67 mole) of hydroxylamine hydrochloride (Org. Syn. Coll. Vol. I, **1941**, 318) in 240 cc. of methyl alcohol, and of 56.1 g. (1 mole) of c.p. potassium hydroxide in 140 cc. of methyl alcohol, are prepared at the boiling point of the solvent. Both are cooled to 30–40° (Note 1), and the one containing alkali is added with shaking to the hydroxylamine solution; any excessive rise of temperature during the addition is prevented by occasional cooling in an ice bath. After all the alkali has been added, the mixture is allowed to stand in an ice bath for five minutes to ensure complete precipitation of potassium chloride. Fifty grams (0.33 mole) of ethyl benzoate is added with thorough shaking, and the mixture filtered immediately with suction. The residue in the funnel is washed with a little methyl alcohol. The filtrate is placed in an Erlenmeyer flask and allowed to stand at room temperature. Crystals begin to form within twenty minutes to three hours, depending upon the amount of supersaturation of the solution. After forty-eight hours the crystals are filtered, washed with a little absolute ethyl alcohol, and dried in air. The yield is 33–35 g. (57–60 per cent of the theoretical amount) (Note 2), (Note 3), and (Note 4).

(*B*) *Benzohydroxamic Acid*.—A mixture of 35 g. (0.2 mole) of the potassium salt in 160 cc. of 1.25 *N* acetic acid is stirred and heated until a clear solution is obtained. The solution is allowed to cool to room temperature and finally chilled in an ice bath. Benzohydroxamic acid separates as white crystals. After filtering and drying, the product melts at 120–128° and weighs 25–26 g. (91–95 per cent of the theoretical amount). The crude material may be purified by dissolving it in 4.5 times its weight of hot ethyl acetate, filtering from a small amount of solid, and allowing the solution to cool to room temperature. The white crystals which separate are filtered, washed with a little benzene, and allowed to dry in air. The yield of recrystallized product, m.p. 125–128°, from 26 g. of crude material is 20 g. (77 per cent recovery) (Note 5).

2. Notes

1. The hydroxylamine hydrochloride solution should not be cooled too quickly or crystallization may occur before mixing. Exposure to atmospheric oxygen should be minimized after mixing the solutions, to avoid oxidation of the free hydroxylamine.
2. By concentrating the alcoholic mother liquors an additional 3–5 g. of the potassium salt may be obtained.
3. This salt can be used for the preparation of acyl derivatives; for example, when suspended in dioxane and treated with benzoyl chloride, dibenzohydroxamic acid is formed in excellent yield.
4. The potassium salts of *p*-methyl- and *p*-methoxybenzohydroxamic acid have been prepared by the submitters by this method in approximately the same yields.
5. This product has a neutralization equivalent of 137.5–138 (calculated 137.1) when determined as follows. Several drops of an alcoholic solution of 1,3,5-trinitrobenzene are added to 30–40 cc. of water in a flask, and 0.1 *N* alkali (about 0.5 cc.) is run in until a pink color is just produced. An accurately weighed sample (approximately 0.3 g.) of benzohydroxamic acid is then dissolved in the solution and titrated with standard alkali until the pink color is restored. The latter titer is used to calculate the neutralization equivalent.

3. Discussion

Benzohydroxamic acid has been prepared by the action of hydroxylamine on benzoyl chloride,[1] ethyl benzoate,[2], [3] or benzamide.[4]

References and Notes

1. Lossen, Ann. **161**, 347 (1872); Jones and Hurd, J. Am. Chem. Soc. **43**, 2446 (1921)
2. Renfrow and Hauser, ibid. **59**, 2312 (1937).
3. Tiemann and Krüger, Ber. **18**, 740 (1885); Jeanrenaud, ibid. **22**, 1272 (1889).
4. Hofmann, ibid. **22**, 2856 (1889).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

dibenzohydroxamic acid

potassium salts of p-methyl- and p-methoxybenzohydroxamic acid

ethyl alcohol (64-17-5)

acetic acid (64-19-7)

Benzene (71-43-2)

ethyl acetate (141-78-6)

methyl alcohol (67-56-1)

oxygen (7782-44-7)

benzoyl chloride (98-88-4)

benzamide (55-21-0)

potassium hydroxide (1310-58-3)

ethyl benzoate (93-89-0)

1,3,5-Trinitrobenzene (99-35-4)

Hydroxylamine hydrochloride (5470-11-1)

hydroxylamine (7803-49-8)

potassium salt (140-89-6)

potassium chloride (7447-40-7)

Benzohydroxamic acid (495-18-1)

Potassium Benzohydroxamate (32685-16-8)

dioxane (5703-46-8)