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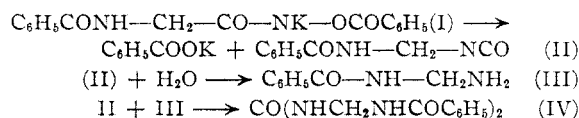
## The Rearrangement of Aminoacetohydroxamic Acid

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The rearrangement of aliphatic  $\alpha$ -amino hydroxamic acids has not been studied. In fact, only one such compound has been reported,<sup>2</sup> namely, aminoacetohydroxamic acid.

Some precedent is at hand, however, since glycolohydroxamic<sup>3a</sup> and other  $\alpha$ -hydroxy hydroxamic acids<sup>3b</sup> have been studied. Potassium glycolobenzoylhydroxamate,  $\text{HOCH}_2\text{CHNKCOCOC}_6\text{H}_5$ , failed to rearrange in hot water but it did rearrange into isopentyl allophanate and formaldehyde on boiling in isopentyl alcohol, suggesting that the anticipated hydroxymethyl isocyanate,  $\text{HOCH}_2\text{NCO}$ , decomposes at once into formaldehyde and cyanic acid. The lactic and mandelic analogs underwent rearrangement in hot water. The products included not only the expected aldehydes (acetaldehyde, benzaldehyde) but also *sym*-dibenzoylurea.

In the present work aminoacetohydroxamic acid was prepared, benzoylated and rearranged. Benzoylation gave rise to hippurobenzoylhydroxamic acid. Its potassium salt (I), when heated in water, decomposed to yield a compound which proved to be *N,N'*-bis-(benzamidomethyl)-urea (IV). There was no evidence for dibenzoylurea, an allophanic derivative, or methyleneurea. The last might have resulted if aminomethyl isocyanate,  $\text{H}_2\text{NCH}_2\text{NCO}$ , were an intermediate product. The reaction observed is covered by the following equations.



## Experimental

Analyses reported herein were performed by Margaret Ledyard and Patricia Craig. Aminoacetohydroxamic acid, m.p. 142–143° (dec.), was prepared by the method of Jones

(1) Holder of Swift and Company post-doctoral fellowship, 1946–1947.

(2) Jones and Sneed, *This Journal*, **39**, 673 (1917).

(3) (a) Jones and Powers, *ibid.*, **46**, 2518 (1924); (b) Jones and Neuffer, *ibid.*, **39**, 659 (1917).

and Sneed<sup>2</sup> who reported a m.p. of 140°. Seven grams was obtained from an original 14 g. of glycine ethyl ester hydrochloride.

**Benzoylation.**—There was added dropwise 9.3 g. (7.7 cc.) of benzoyl chloride into a stirred, aqueous solution containing 2 g. of potassium hydroxide and 3 g. of aminoacetohydroxamic acid. The mixture was cooled to 0–5°. The white precipitate was collected on a filter, washed with water, dried, and crystallized from chloroform; yield 3.5 g.; m.p. 159°.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$ : N, 9.39. Found: N, 9.26.

**Potassium Hippurobenzoylhydroxamate (I).**—Fifteen minutes after mixing 5.5 g. of hippurobenzoylhydroxamic acid (100 cc. absolute alcohol, 15 cc. absolute ether) and 0.14 g. of potassium hydroxide (16 cc. absolute alcohol) a precipitate started to form. The yield was 3 g. after ten hours at 5°. It changed color without melting at about 110°.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{13}\text{KN}_2\text{O}_4$ : N, 8.75. Found: N, 8.36.

**Rearrangement.**—Half a gram of the potassium salt was dissolved in 30 cc. of water, filtered for complete clarity, and the clear solution was heated to boiling. Precipitation occurred within a few minutes; m.p. 246–246.5°. The recorded value<sup>4</sup> for *N,N'*-bis-(benzamidomethyl)-urea is 246°. Analysis also was satisfactory.

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2$ : N, 17.17. Found: N, 17.14.

Under the polarizing microscope this material appeared as microscopic needles. Curtius<sup>4</sup> also described it as microscopic needles. In this respect it differs from methyleneurea, m.p. 240–250°. The latter was prepared following Dixon's directions.<sup>5</sup> Under the polarizing microscope the latter appeared as an amorphous powder, showing black crosses under crossed nicols, thereby resembling starch in this respect.

The rearrangement product did not depress the m.p. of authentic *N,N'*-bis-(benzamidomethyl)-urea, but also it failed to depress the m.p. range of the methyleneurea. Hence, mixed m.p. determinations were considered unreliable for this characterization.

## Summary

The benzoyl derivative of aminoacetohydroxamic acid undergoes a normal Lossen rearrangement to form *N,N'*-bis-(benzamidomethyl)-urea.

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(4) Curtius, *J. prakt. Chem.*, [2] **87**, 520 (1913).

(5) Dixon, *J. Chem. Soc.*, **113**, 239 (1918).