[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE KETAZINES OF LEVULINIC ACID AND OF LEVULINIC HYDRAZIDE

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Having occasion to prepare the hydrazone of fluorenonecarboxylic acid-2, it was thought best to gain experience by preparing the hydrazone of a less expensive keto acid. Levulinic acid was selected. So far as could be determined, no keto acid hydrazone has ever been obtained. Curtius[1] attempted the preparation of the hydrazone of pyruvic acid, $CH_3COCOOH$. He treated barium pyruvate with hydrazine sulfate and did not obtain the hydrazone, but instead a compound of unknown structure, of empirical composition, $C_6H_{10}N_2O_3$. When he treated the free acid with hydrazine hydrate, he obtained the hydrazine salt of the hydrazone. He was unable to prepare the acid hydrazone from this. The reason seems apparent from the results reported in this article.

Later,[2] in working with ethyl levulinate, he found that hydrazine hydrate converts it into the hydrazide of levulinic acid, $CH_3COCH_2CH_2CONHNH_2$, m. p. 82°, just as ammonia converts an ester into an amide. The ketonic group is apparently untouched.

It is also generally known that any organic acid if boiled with hydrazine hydrate forms the hydrazide.

$$RCOOH + N_2H_5OH = RCONHNH_2 + 2H_2O$$

It would be necessary, therefore, in preparing the hydrazone of levulinic acid to cover the carboxyl group to prevent the formation of the hydrazide. The sodium salt of the acid was treated with hydrazine hydrate and then carefully acidified to obtain the free acid. In ten reactions under various conditions no hydrazone was found, but in all cases various amounts were formed of the ketazine of levulinic acid, $HOOCCH_2CH_2C(CH_3){=}N{-}N{=}C(CH_3)CH_2CH_2COOH$.

The ketazine is a new compound. It is very easily hydrolyzed in hot water and slowly even by the moisture of the air, since it is very hygroscopic. The hydrolytic products are the hydrazide and free levulinic acid.

Experiments starting with the free acid and also with the hydrazide resulted in the formation of the ketazine of the hydrazide in both cases and none of the salt nor of the hydrazone was obtained.

Attempts to Prepare the Hydrazone of Levulinic Acid.—To a solution of 2 g. of sodium in 25 cc. of 95% alcohol, 10 g. of levulinic acid was added. After five minutes, 15 cc. of 40% hydrazine hydrate was added and the mixture refluxed for sixteen hours

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[1] Curtius, *J. prakt. Chem.*, [2] **44**, 555 (1891).

[2] Curtius, *ibid.*, [2] **50**, 522 (1894).

on a water-bath. The alcohol, water and excess hydrazine hydrate were now distilled at reduced pressure and the dry salt dissolved in a very small amount (10 cc.) of ice water. Then slowly, cooling with an ice and salt mixture, 22 cc. of 6 *N* hydrochloric acid was added from a buret. A white precipitate began to form and quickly increased in amount until 6.5 g. was obtained, of melting point 112–114°. This represents a 58% yield of the ketazine of levulinic acid.

A second run, in which the precipitate was washed more carefully, yielded 4 g. melting at 119–120° (corr.). It was insoluble in ether or petroleum ether and practically insoluble in cold alcohol or water. On boiling with either of the latter, however, it is quantitatively changed to the hydrazide of levulinic acid, m. p., 81–82°, and levulinic acid. It is also very hygroscopic and is almost completely hydrolyzed in a few days by the moisture thus absorbed.

Anal. Calcd. for $C_{10}H_{16}O_4N_2$: N, 12.28. Found: 12.36.

Mol. wt. By titration: calcd.: 228. Found: 230.

Attempts to Prepare the Hydrazone of the Hydrazide of Levulinic Acid.—In a 200 cc. round-bottomed flask fitted with a reflux condenser, 10 cc. of 50% hydrazine hydrate was placed and then slowly from a dropping funnel, 6.5 g. of the hydrazide of levulinic acid in 16 cc. of alcohol was added. The mixture was then refluxed for twenty hours. The solution was filtered and allowed to cool, whereupon colorless crystals melting at 217–219° (corr.) were obtained. Later the following simpler method was used.

A solution of 11.6 g. of levulinic acid in 5 cc. of alcohol was added to 35 cc. of 50% hydrazine hydrate on a water-bath. After twenty hours' refluxing and proceeding as above, a white crystalline solid amounting to 1 g. was obtained. After boiling up twice with absolute alcohol to remove impurities, a product insoluble in alcohol, water, ether, etc., melting at 219–220° (corr.) resulted. It is identical with that formed from the hydrazide, as is shown by a mixed melting point test. The product is neutral and does not blacken yellow mercuric oxide, reduce Fehling's solution, nor form a condensation product with benzaldehyde, thus showing that it is neither a hydrazine salt nor a hydrazone. The analysis showed it to be the ketazine of the hydrazide of levulinic acid, the formula of which is $NH_2NHCOCH_2CH_2C(CH_3){=}N{-}N{=}C(CH_3)CH_2CH_2CONHNH_2$.

Anal. Calcd. for $C_{10}H_{20}O_2N_6$: N, 32.81. Found: 32.30.

Mol. wt. By freezing point depression of glacial acetic acid, calcd.: 256. Found: 254.8.

This work was undertaken at the suggestion of Professor W. A. Noyes.

Summary

1. Attempts to prepare the hydrazone of levulinic acid resulted in the formation of the ketazine of the acid.

2. Attempts to prepare the hydrazone of the hydrazide of levulinic acid and also of the hydrazine salt of the acid resulted in the formation of the ketazine of levulinic hydrazide.

3. The following new compounds were prepared: (a) the ketazine of levulinic acid, $C_{10}H_{16}O_4N_2$, m. p. 119–120° (corr.); (b) the ketazine of levulinic hydrazide, $C_{10}H_{20}O_2N_6$, m. p. 219–220° (corr.).

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