Experimental

dl-**Hydantoin-5-propionic Acid (III).**—Hydantoin-5-propionic acid was prepared in a 62% yield from sodium glutamate and potassium cyanate according to the directions of Dakin.[1] After recrystallization from water, the product melted at 170°.[4]

Hydantoin-5-propiolactam-1 (IV).—Hydantoin-5-propionic acid (1.7 g.) was refluxed for two hours in 15 cc. of xylene containing 0.5 g. of phosphorus pentoxide. The mixture was allowed to stand overnight and crystals separated. The solvent was decanted and the crystals washed with 10 cc. of cold methanol and then recrystallized from 70% methanol. The yield was 1.2 g. (78%) of product melting at 196–198°. After three recrystallizations the substance melted sharply at 201°.

Anal. Calcd. for $C_6H_6O_3N_2$: C, 46.75; H, 3.92; N, 18.18. Found: C, 46.87; H, 4.12; N, 18.25.

1-Acetyl-hydantoin-5-propiolactam-1 (V).—A mixture of hydantoin-5-propionic acid (5 g.) and acetic anhydride (25 cc.) was refluxed for one hour. The excess solvent was removed by distillation *in vacuo* and the residue was crystallized by the addition of alcohol. Recrystallization from alcohol yielded 5 g. (88%) of product melting at 147–148°. One gram of this product was refluxed for four hours with acetic anhydride and recovered unchanged.

Anal. Calcd. for $C_8H_8O_4N_2$: C, 48.98; H, 4.11. Found: C, 48.96; H, 4.31.

Acetylation of Hydantoin-5-propiolactam-1.—Twenty-five mg. of hydantoin-5-propiolactam-1 was acetylated under the same conditions as the hydantoin-5-propionic acid and yielded a product melting at 147–148°. A mixed melting point with the product obtained by the acetylation of hydantoin-5-propionic acid showed no depression.

2-Thiohydantoin-5-propiolactam-1 (VIII).—Pyrrolidone carboxylic acid (VII) (40 g.) (from glutamic acid) and 28 g. of ammonium thiocyanate were warmed on a steam-bath with 180 cc. of acetic anhydride and 20 cc. of glacial acetic acid. A red solution was obtained which yielded 22 g. (43%) of crystals (m. p. 206–207°) after the addition of benzene. The recorded m. p. is 206–207°.

2-Thiohydantoin-5-propionic Acid (IX).—Two grams of (VIII) was refluxed with 25 cc. of 1 *N* hydrochloric acid for one-half hour and cooled. Two grams (90%) of acid (IX) melting at 121.5–122° crystallized out. The recorded m. p. is 122°.

Dehydration of 2-Thiohydantoin-5-propionic Acid (IX).—Two hundred mg. of IX was refluxed for two hours with 15 cc. of toluene containing 100 mg. of phosphorus pentoxide. The solvent was decanted while hot from a small amount of brown residue. On cooling crystals separated from the toluene solution. The yield was 120 mg. (66%) melting at 206–207°. A mixed m. p. with the lactam (VIII) gave no depression.

Acknowledgment.—We wish to thank Mr. John M. Kolbas for his assistance in the preparation of the manuscript.

Summary

The products obtained by the dehydration and the acetylative dehydration of hydantoin-5-propionic acid have been shown to possess the lactam structure IV and V.

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(4) All melting points were recorded on a micro stage and are uncorrected.

NOTES

Synthesis of Bromoacetals

BY PAUL Z. BEDOUKIAN

Of the many syntheses of bromoacetal reported, that of Filachione[1] is the most convenient. It consists of slow addition of bromine to a mixture of vinyl acetate and alcohol at very low temperature (−40°). A recent modification of this method[2] involves very slow addition (ten hours) of bromine in the vapor form to a well-cooled mixture of vinyl acetate and alcohol.

The yields in both procedures are not high, being 46% for dimethyl acetal and 58–68% for diethyl acetal, and the method is rather cumbersome and time-consuming. Its chief disadvantage appeared to be the presence of methyl or ethyl alcohol during the bromination reaction, necessitating slow addition of bromine at low temperatures in order to prevent the bromination of the alcohol.

When bromine is added to a mixture of vinyl acetate and carbon tetrachloride at 0–10°, addition is very rapid and in the theoretical quantities. On adding the mixture to methyl or ethyl alcohol (99.5–100%) with cooling, a rapid reaction takes place with the formation of bromoacetal. This method is applicable to small or large scale preparations and the yields are of the order of 80–85% for dimethyl acetal and 75–80% for diethyl acetal.

Contrary to previous reports, bromoacetal freed from traces of bromoacetaldehyde by means of bisulfite or fractionation is not a lachrymator but does possess a rather pungent odor. On standing for several weeks a slight decomposition takes place with the formation of bromoacetaldehyde.

Experimental

Preparation of Bromoacetaldehyde Dimethyl Acetal.—One mole of vinyl acetate (86 g.) b. p. 71–73° was added to 150 ml. of carbon tetrachloride and cooled in an ice–water mixture. A mixture of 90 ml. of carbon tetrachloride and 160 g. of bromine was added to the vinyl acetate mixture with shaking, care being taken not to allow the temperature to rise above 10°. The addition took about twenty minutes and the end-point was reached when bromine no longer decolorized. The brominated mixture was then added to 350 ml. of methyl alcohol (99.5–100%), and cooled during the first hour to prevent rise in temperature as bromoacetal is formed. It was shaken occasionally and allowed to stand for two days. The mixture which consisted of two layers was diluted with one liter of water and the bromoacetal–carbon tetrachloride layer drawn off. The methyl alcohol–water mixture was further ex-

(1) Filachione, THIS JOURNAL, **61**, 1705 (1939).

(2) "Organic Syntheses," **23**, 8 (1943).

tracted twice with 150 ml. of carbon tetrachloride to recover the major portion of the dissolved bromoacetal. The carbon tetrachloride solutions were combined and distilled through a Whitmore-Fenske type column. Bromoacetaldehyde dimethyl acetal (124 g. or 83%) distils at 48–49° (14 mm.), $n^{20}D$ 1.4450; d^{20}_4 1.430.

Preparation of Bromoacetaldehyde Diethyl Acetal.—The above procedure was repeated using 500 ml. of ethyl alcohol (99.5–100%) instead of 350 ml. of methyl alcohol. Distillation yielded bromoacetaldehyde diethyl acetal (151 g. or 77%), b. p. 64–65° (16 mm.), $n^{20}D$ 1.4418; d^{20}_4 1.280. On using commercial 95% ethyl alcohol the yield was somewhat lower (142 g. or 72%).

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An Improved Method for the Synthesis of Quinone

BY JOHN H. BILLMAN, BERNARD WOLNAK AND DAVID K. BARNES

In the course of another investigation it was necessary to prepare quinone in relatively large amounts. The procedure described in "Organic Syntheses"[1] requires vanadium pentoxide as a catalyst. Since there was no vanadium pentoxide available, we substituted an equivalent amount of ammonium metavanadate which worked equally well and gave comparable yields. In addition the reaction time was reduced to less than one third the time normally required. Other runs were made using increased amounts of ammonium metavanadate and warming the reaction mixture to 40° before adding the catalyst. It was found that the greater the amount of catalyst used the faster the reaction proceeded. Thus with 1.4 g. of ammonium metavanadate the reaction was complete in less than half an hour or about one-eighth the time normally required. The final procedure which was used is described in the experimental part.

Experimental

Quinone.—In a 2-liter round-bottom three-neck flask equipped with a mechanical stirrer and a thermometer were placed 1 liter of a 2% sulfuric acid solution, 110 g. of hydroquinone, and 60 g. of sodium chlorate. The mixture was vigorously stirred and warmed to 40°. At this temperature 1.4 g. of ammonium metavanadate was added. The flask was cooled from time to time, with tap water, so that the temperature did not rise above 42°. The reaction was over in less than thirty minutes. The mixture was cooled to 10°, then filtered with suction, and the quinone washed once with 100 ml. of cold water. After drying in a desiccator over calcium chloride the product weighed 97–99 g. and melted at 112–113°. Extraction of the filtrate and washings with three 100-ml. portions of warm benzene yielded 3–4 g. more of quinone, bringing the total amount to 101–103 g. (93–95% of the theoretical amount).

The quinone may be dried in about an hour in an oven at 100°. This should be done under a hood. There is about a 15% loss due to sublimation. Over calcium chloride, it takes from one to two days for the quinone to dry.

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(1) "Organic Syntheses," Coll. Vol. II, 1943, p. 553.

Preparation of *o*-Aminobenzyl and β-Aminoethyl Thiazolium Salts

BY HANS T. CLARKE

In view of the interesting observations recorded by Sealock and Goodland,[1] a description becomes necessary of the preparation of the thiazolium amino compounds which inhibit the enzymatic decomposition of the amine. After the recognition of the thiazole ring in thiamine,[2] these substances were synthesized early in 1936 for study as models, but they found useful application only after they had reached Dr. Sealock's Laboratory.

Experimental

3-*o*-Nitrobenzyl-4-methylthiazolium Chloride.—A mixture of 3.5 g. of *o*-nitrobenzyl chloride, 1 cc. of benzene and 2.0 g. of 4-methylthiazole was heated at 95–100° in a sealed tube for eighty to ninety hours. The crystalline product, well washed with ether and recrystallized from absolute alcohol, decomposed at 186.5–187°. The yield was 4.1 g. or 75%.

Anal. Calcd. for $C_{11}H_{11}O_2N_2SCl$: N, 10.4; Cl, 13.1. Found: N, 10.04; Cl, 13.1.

3-*o*-Aminobenzyl-4-methylthiazolium Chloride Hydrochloride.—A hot solution of 1.4 g. of the above nitro compound in 50 cc. of 2 *N* hydrochloric acid was boiled gently for an hour in the presence of 2.4 g. of granulated tin. As very little action had occurred, 3.4 g. of crystallized stannous chloride was added. The precipitate which formed slowly dissolved in the boiling mixture. The clear solution was warmed at 50° overnight, when most of the tin dissolved. The mixture was diluted, freed of tin salts with hydrogen sulfide and evaporated to dryness under reduced pressure. The residue was warmed with 4 cc. of absolute alcohol, when it rapidly became crystalline; it was filtered and washed with absolute alcohol. The product (about 0.9 g.) after recrystallization from aqueous alcohol decomposed over the range 204–212°.

Anal. Calcd. for $C_{11}H_{14}N_2SCl_2 \cdot H_2O$: C, 44.8; H, 5.1; N, 9.5; Cl, 24.1. Found: C, 45.3; H, 4.9; N, 9.2; Cl, 24.4.

3-β-Phthalimidoethyl-4-methylthiazolium Bromide.—Equimolecular quantities of β-bromoethylphthalimide and 4-methylthiazole were heated in a sealed tube at 95–100° for ten days, when the mixture had completely solidified. The product was washed with ether, and recrystallized from water as platelets, m. p. 238° with slight darkening.

Anal. Calcd. for $C_{14}H_{13}O_2N_2SBr$: N, 7.9; Br, 22.7. Found: N, 7.9; Br, 22.4.

3-β-Aminoethyl-4-methylthiazolium Bromide Hydrobromide.—A solution of 2.5 g. of the phthalimide thiazolium bromide in 10 cc. of 48% hydrobromic acid was boiled under reflux for forty hours, and allowed to cool to room temperature. The phthalic acid (1.0 g., 85%) was filtered off and washed with water; the filtrate and washings were combined and evaporated nearly to dryness, the residue treated with absolute alcohol, and the crystalline product well washed with absolute alcohol. It shrank at 218.5–219.5° and melted with decomposition at 222.5–223.5°; yield 2.1 g.

Anal. Calcd. for $C_6H_{12}N_2SBr_2$: N, 9.2; S, 10.5; Br, 52.7. Found: N, 9.1; S, 10.7; Br, 52.8.

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(1) Sealock and Goodland, THIS JOURNAL, **66**, 507 (1944).
(2) Clarke and Gurin, *ibid.*, **57**, 1876 (1935).