[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

Investigations in the Retene Field. V. The Structure of 6-Acetylretene

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In view of the significance of acetylretene[2] as an intermediate for work in progress at present and in prospect for the future, it was very essential that the position of the acetyl group in acetylretene be determined. By means of a series of steps outlined below, acetylretene was converted into 6-acetoxyretene,[3,4] thus defining the position of the acetyl group as position 6. The structures of derivatives prepared in the past from 6-acetylretene, most notably 6-retenecarboxylic acid and octahydroretene-6-carboxylic acid, are therefore defined.[2,5]

6-Acetylretene oxime[2] was rearranged to 6-acetylaminoretene by means of the well-known Beckmann rearrangement. The latter compound was hydrolyzed by means of alcoholic potassium hydroxide and the 6-aminoretene thus formed was converted into 6-retenol through the agency of the diazo reaction. 6-Retenol was acetylated and both the acetylated product, 6-acetoxyretene, and the parent phenol were found to be identical with authentic specimens of the materials prepared by other means.[3,4]

In addition, the yield of 6-acetylretene obtained from retene, acetyl chloride and aluminum chloride in carbon disulfide solution has been increased to 60%.

The synthesis of 6-retenecarboxylic acid[4,5] has now been simplified considerably. By means of the well-known haloform reaction,[6] 6-acetylretene is smoothly oxidized to 6-retenecarboxylic acid. It is believed that this acid will be a useful intermediate in the synthesis of a true aporesin acid of the abietic series.

Acknowledgments.—We are indebted to Dr. Torsten Hasselstrom for authentic samples of 6-retenol and 6-retenecarboxylic acid.

Experimental

6-Acetylretene.—The procedure followed was essentially that of Bogert and Hasselstrom[2] with the following modifications. The retene used was dissolved in dry carbon disulfide and the solution was allowed to stand over anhydrous calcium chloride to remove the last trace of alcohol which adheres to the hydrocarbon very tenaciously after recrystallization. Instead of converting the crude 6-acetylretene directly to the picrate, as suggested by Bogert and Hasselstrom,[2] the material was distilled *in vacuo*. A pale-yellow, viscous oil came over at 246–251° (corr.) at 3 mm. (metal bath, 300°). The average yield was 60%. This oil crystallized very slowly. If a crystalline product was desired immediately, the oil was converted to the picrate and the latter hydrolyzed. This yielded a cream-colored 6-acetylretene which, after a single crystallization from 95% ethanol (norite), was white and melted at 99.5–100° (corr.).

6-Acetylaminoretene.—To a solution of 2 g. of 6-acetylretene oxime in 30 cc. of absolute ether, there was added in small portions and with vigorous shaking 3 g. of pulverized phosphorus pentachloride. The mixture was allowed to stand for an hour and the ether was evaporated. The residue was treated with cracked ice and the solid thus formed was washed with a 10% sodium carbonate solution. After filtration and drying, the material (2 g.) was recrystallized from toluene, from which it appeared as fluffy white tufts of crystals, m. p. 240–240.5° (corr.), with decomposition.

Anal. Calcd. for $C_{20}H_{21}ON$: C, 82.42; H, 7.27. Found: C, 81.92; H, 7.27.

6-Aminoretene.—A suspension of 0.5 g. of 6-acetylaminoretene in 25 cc. of 95% ethanol containing 2 g. of potassium hydroxide was refluxed for two hours. The solid gradually went into solution. Dilution of the cooled solution produced a white precipitate in stoichiometric yield. Recrystallized from 95% ethanol, the amine appeared as shiny, white plates, m. p. 139.5–140° (corr.).

Anal. Calcd. for $C_{18}H_{19}N$: C, 86.69; H, 7.69. Found: C, 86.61; H, 7.67.

When 6-aminoretene was refluxed with acetic anhydride in the presence of anhydrous sodium acetate, 6-acetylaminoretene resulted; yield, practically that calculated. Recrystallized from toluene, it appeared as fluffy, white tufts of crystals, m. p. 240–241° (corr.). A mixed melting point with an authentic specimen showed no depression.

6-Retenol.—One and three-tenths grams of 6-aminoretene was dissolved in 75 cc. of hot acetic acid and, after cooling, 15 cc. of water was added. To the well stirred suspension of this acetate, there was added dropwise a cold, saturated solution of 2 g. of sodium nitrite, the temperature being maintained between 0 and 5°. The suspension changed immediately to a clear solution. After being stirred for fifteen minutes, the cold solution was slowly poured into a hot solution of 10 g. of concentrated sulfuric acid and 5 g. of sodium sulfate in 30 cc. of water. The resulting mixture was heated near the boiling point until the evolution of gases ceased. Dilution of the cooled solution yielded crimson crystals (1.1 g.). An alternative method of decomposing the diazonium salt lay in adding an excess of urea to destroy the unreacted nitrous acid fol-

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(1) Fritzsche Fellow in Organic Chemistry, Columbia University, 1935–1936.

(2) Bogert and Hasselstrom, THIS JOURNAL, **53**, 3462 (1931).

(3) Fieser and Young, *ibid.*, **53**, 4120 (1931).

(4) Komppa and Wahlforss, *ibid.*, **52**, 5009 (1930).

(5) Bogert and Hasselstrom, *Proc. Nat. Acad. Sci.*, **18**, 417 (1932).

(6) Fuson and Tullock, THIS JOURNAL, **56**, 1638 (1934).

lowed by heating on the steam-bath. Inasmuch as 6-retenol is very difficultly soluble in aqueous alkali, these crystals were dissolved in hot, alcoholic potassium hydroxide and reprecipitated by means of concentrated hydrochloric acid. When the finely-divided, red solid thus obtained was boiled with a large volume of dilute potassium hydroxide, the greater portion of the material dissolved to a bright red solution. Acidification of the latter yielded a pale-yellow precipitate which, after filtration and drying, was recrystallized from xylene, giving slightly yellow scales, m. p. 163.5–164.5° (corr.). Mixed with an authentic specimen of 6-retenol, m. p. 162.5–163° (corr.), it melted at 162.5–163° (corr.).

6-Acetoxyretene.—6-Retenol was acetylated by means of acetic anhydride in the presence of anhydrous sodium acetate; white, silky needles from dilute ethanol, m. p. 133–133.5° (corr.). A mixture of this and an authentic specimen of 6-acetoxyretene of m. p. 134–135° (corr.) melted at 133–133.5° (corr.).

6-Retenecarboxylic Acid.—To a solution of 2 g. of 6-acetylretene in 100 cc. of dioxane and 20 cc. of 10% sodium hydroxide, there was added in small portions with shaking an aqueous solution of iodine in potassium iodide.[6] When the iodine color persisted at 60° for two minutes, excess sodium hydroxide was added and the solution was cooled. After dilution, the iodoform was filtered off and the filtrate acidified. A yellow precipitate formed. After drying at 110°, this solid (1.5 g.) was boiled with dilute potassium hydroxide (norite), reprecipitated with dilute acid, dried, and recrystallized from benzene, from which it appeared as small, white needles, m. p. 238–238.5° (corr.). Mixed with an authentic specimen of 6-retenecarboxylic acid of m. p. 238–238.5° (corr.), it melted at 236–237° (corr.).

Summary

1. The structure of 6-acetylretene has been established.

2. The synthesis of 6-retenecarboxylic acid from 6-acetylretene has been simplified by the use of an alkaline iodine–potassium iodide solution as the oxidant.

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Preparation of Macrocyclic Lactones by Depolymerization[1]

BY E. W. SPANAGEL AND W. H. CAROTHERS

Lactones of the higher ω-hydroxy fatty acids were first successfully synthesized by oxidizing the corresponding cyclic ketones.[2] Preparation by the conventional methods is impossible because the acids tend to react intermolecularly yielding linear polyesters. Once this fact was clearly recognized it became evident[3] (p. 2551) that direct lactonization might be favored by application of the dilution principle first utilized by Ruggli;[4] and Stoll and Rouvé[5] have showed experimentally that this is indeed the case.

A third method for the preparation of large ester rings consists in depolymerizing the corresponding linear polyester. This was first realized with esters of carbonic and oxalic acids.[6] Later it was shown that, by the proper control of temperature and selection of catalysts, excellent results could also be obtained with glycol esters of other dibasic acids.[7]

We have now applied this method to the preparation of several lactones. The possibilities are indicated by the fact that a 70% yield of pure monomer was obtained from the polyester of hydroxytetradecanoic acid. Stoll and Rouvé[5] in a similar case report yields by the dilution method considerably higher than this, but their scale of operation was small (10 g.), the volume large (10 liters) and the time long (six days). Our depolymerization required only three and one-half hours for 32 g. of polyester. It appears therefore that this method has some advantages over the use of high dilution.

One of the objects of the present work was to obtain some lactones which had not been reported previously. Meanwhile Stoll and Rouvé have published a much more extended study[5] of lactonization by the dilution method covering in part the same ground. The overlapping results of the two investigations are in good agreement, but in several cases we are able to report slightly higher melting points than were found by Stoll and Rouvé.

As new compounds we report

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(1) Paper XXVIII on Polymerization and Ring Formation; Paper XXVII, THIS JOURNAL, **57**, 1131 (1935).

(2) Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).

(3) Carothers, THIS JOURNAL, **51**, 2548 (1929).

(4) Ruggli, *Ann.*, **392**, 92 (1912).

(5) Stoll and Rouvé, *Helv. Chim. Acta*, **17**, 1283 (1934).

(6) Hill and Carothers, THIS JOURNAL, **55**, 5031 (1933).

(7) Spanagel and Carothers, *ibid.*, **57**, 929 (1935).