

five days, respectively. The alkali originally added was neutralized with equivalent amounts of sulfuric acid, and the reaction mixtures were filtered, combined, and concentrated *in vacuo* in a water-bath at 50° to a thick sirup. Extraction of the sirup with methanol was carried out according to the directions of Pigman,⁵ the extracts being combined and treated with 30 g. of decolorizing carbon. The colorless filtrate was concentrated *in vacuo* on a water-bath at 40° to a thick sirup. Ethanol (25 ml.) was added and the solution was seeded and reconcentrated *in vacuo* at room temperature for eighteen hours or until the mass had become crystallized. The crystalline mass was then triturated with 150 ml. of methanol-ethanol (60/40) and allowed to stand at -30° for twenty-four hours, yielding 248 g. (74%) of the uronic acid monohydrate. The galacturonic acid was of good purity, sintering at 108-110° and exhibiting a specific rotation $[\alpha]^{20}_D +50.3^\circ$ (*c*, 4) in water.

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The Formation of Ergostatetraene-B During the Acetylation of Ergosterol

BY HARRY A. STANSBURY, JR.

It has been frequently observed in this Laboratory that the acetylation of ergosterol by means of boiling acetic anhydride gives an unsatisfactory yield of ergosteryl acetate, and that the physical properties of the crude product indicate the presence of low melting by-product of positive optical rotation. This by-product has now been shown to be a hydrocarbon formed by the dehydration of ergosterol. It is identical with ergostatetraene-B, which had previously been prepared by the action of acetic anhydride¹ or maleic anhydride² on ergostatetraene-A, and by the dehydration of ergosterol with *p*-toluenesulfonyl chloride in pyridine.²

Experimental

In a typical experiment 200 g. of ergosterol was refluxed for thirty minutes with 2 liters of acetic anhydride. After cooling the crude acetate was filtered, washed with glacial acetic acid and methanol, and recrystallized from ethyl acetate. A total of 160 g. of ergosteryl acetate of m. p. 171° was thus obtained. The mother liquor from this crystallization was concentrated to a small volume, and then diluted with ethanol. Upon cooling, 3.5 g. of fine, colorless needles was obtained which after recrystallization from ether-alcohol showed m. p. 101.5° and $[\alpha]^{25}_D +97^\circ$. *Anal.* Calcd. for C₂₈H₄₂: C, 88.8; H, 11.2. Found: C, 88.7; H, 11.0. When mixed with an authentic sample of ergostatetraene-B, m. p. 101-101.5°; $[\alpha]^{25}_D +100^\circ$, prepared according to the directions of Stoll,² the hydrocarbon showed no depression of the melting point. Fractional recrystallization of the ergosterol used in the present

experiments failed to reveal the presence of this hydrocarbon.

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Catalytic Degradation of Heptaldehyde in Vapor Phase

BY T. J. SUEN AND SIMONE FAN

In a previous paper¹ the authors reported that when heptaldehyde was hydrogenated with a nickel catalyst at 250° under atmospheric pressure, *n*-hexane was obtained, together with some *n*-heptyl alcohol. In order to ascertain whether the presence of hydrogen is essential for the degradation reaction, heptaldehyde was pyrolyzed over the nickel catalyst without the admixture of hydrogen. The experimental procedure and operating conditions were the same as described previously, except that an additional trap filled with active carbon was inserted between the first trap and the wet gas meter to retain the hydrocarbon vapor uncondensed. It was subsequently stripped with live steam and combined with the other portions of the liquid products.

When analyzing the liquid products, it was found that a considerable amount of unsaturated hydrocarbons was present, and their content was determined in the following manner. Ten ml. of the liquid product fractionated over between 66-70° was shaken with 30 ml. of 96% sulfuric acid for about five minutes in a glass-stoppered buret. After standing, the volume of the oil layer was read. The decrease in volume was considered as the content of the unsaturated hydrocarbons. It was noted that the refractive index of the liquid was lowered by the acid treatment, and this agrees with the assumption that unsaturates were present.² The treated and redistilled product gave physical constants essentially the same as those of *n*-hexane.

It was also observed that when no hydrogen was used during the reaction, the catalyst deteriorated quite rapidly. The yield of the degradation products became lower and lower. Unreacted heptaldehyde was also found present in the products, as determined by the bisulfite method.³

(1) Suen and Fan, *THIS JOURNAL*, **64**, 1460 (1942).(2) For *n*-hexane, n^{20}_D 1.37506; hexene-1, n^{20}_D 1.3886; hexene-2, n^{20}_D 1.3958; hexene-3, n^{20}_D 1.3942. See Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939.(3) Parkinson and Wagner, *Ind. Eng. Chem., Anal. Ed.*, **6**, 433 (1934).(1) Rhyg, *Z. physiol. Chem.*, **185**, 99 (1929).(2) Stoll, *ibid.*, **202**, 235 (1931).