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 $[\alpha]^{20}\text{D}$ $+50.3°$ (*c*, 4) in water.

ALBANY, CALIFORNIA
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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 anhydride[1] or maleic anhydride[2] 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 $[\alpha]^{25}\text{D}$ $+97°$. *Anal.* Calcd. for $C_{28}H_{42}$: 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°; $[\alpha]^{23}\text{D}$ $+100°$, 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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[1] Rhyg, *Z. physiol. Chem.*, **185**, 99 (1929).

[2] Stoll, *ibid.*, **202**, 235 (1931).

Catalytic Degradation of Heptaldehyde in Vapor Phase

BY T. J. SUEN AND SIMONE FAN

In a previous paper[1] 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]

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[1] Suen and Fan, THIS JOURNAL, **64**, 1460 (1942).

[2] For *n*-hexane, $n^{20}\text{D}$ 1.37506; hexene-1, $n^{20}\text{D}$ 1.3886; hexene-2, $n^{20}\text{D}$ 1.3958; hexene-3, $n^{20}\text{D}$ 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).

TABLE I

RESULTS OF CATALYTIC PYROLYSIS AT 250°

Expt. no.		A	B	C
Catalyst condition, after hrs. use		fresh	1.5	7
Heptaldehyde used, ml.		42.5	47.0	44.2
Org. liq. product, ml.		33.8	41.3	38.5
Liq. b. p. 66–70°, vol. % of liq. prod.		67	62	43
Unreacted aldehyde, wt. % of liq. prod.		..	1.9	15.0
% Unsatd. in 66–70° portion		..	24	30
Gas analysis, %	CO_2	0.8	1.4	0.4
	O_2	5.4	1.6	3.2
	Unsaturates	0.6	1.2	1.8
	CO	48.2	57.4	50.2
	H_2	12.0	..	18.9
	CH_4	13.1	..	14.4
	N_2 (by diff.)	19.9	..	11.1

The results of three typical experiments are given in Table I. The fractionation curves of the liquid products are shown in Fig. 1.

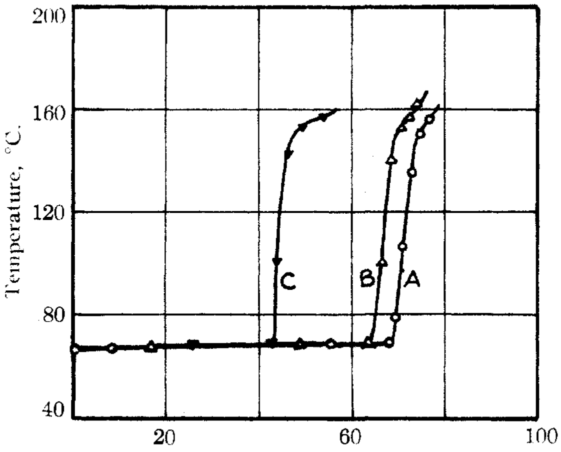

Fig. 1.

The higher-boiling portion of the liquid products was not analyzed in detail, but a rough examination of its boiling range, refractive index, and smell showed that some other compounds were present in addition to *n*-heptyl alcohol.

Experiments at 200° also have been carried out. The reaction did not go very far. Average of two experiments showed that the degradation products *i. e.*, the portion boiling between 66–70°, only amounted to 20% of the liquid products.

The results given above throw some light on the mechanism of the reaction. As indicated in Table I, free hydrogen and methane both were present in the gaseous products, although no hydrogen was primarily added. Furthermore, unsaturated hydrocarbons also were found in the degradation products. Evidently the following reaction takes place during the decomposition

$$C_6H_{13}CHO \longrightarrow C_6H_{12} + CO + H_2 \qquad (1)$$

However, this reaction does not fully account for the large amount of hydrogen and methane obtained, in comparison with hexene. In all the experiments the amount of liquid products collected was always smaller than expected. In other words, a part of the heptaldehyde used, or liquid products obtained therefrom, was decomposed into gases.

With free hydrogen present, as indicated in Equation (1), a part of the hexene formed is reduced to hexane.

$$C_6H_{12} + H_2 \longrightarrow C_6H_{14} \qquad (2)$$

It is of course also possible that hexane is the primary decomposition product, and the hexene is formed through dehydrogenation of hexane

$$C_6H_{14} \longrightarrow C_6H_{12} + H_2 \qquad (3)$$

But reaction (3) is not probable. A perusal of the literature shows that palladium black has a slight dehydrogenation action on *n*-hexane at 300° and, in the presence of nickel and added hydrogen, *n*-hexane decomposes to methane at 400°.[4,5] In the present case, the temperature seems to be too low to cause the dehydrogenation reaction. Furthermore, analysis of the degradation products obtained by decomposing heptaldehyde alone at 200° showed that it contained about 35% of unsaturated hydrocarbons while that obtained at 250° contained about 24–30% as given in Table I. This also indicates the improbableness of the above reaction.

The identity of the unsaturated portion in the degradation products, though not determined, could more or less be inferred from the available data. As its boiling range is within 66–70° (almost nothing in the liquid products was fractionated over below 66°), it is not hexene-1, which has a b. p. of 63.5°.[2] A few degrees difference in boiling temperature could be detected with the fractionating column employed. Hexene-2 and hexene-3, with their respective *cis* and *trans* forms and mixtures, all boil within the range 66–70°. During the decomposition of heptaldehyde, it is more probable that hexene-1 is first formed. However, it is known that α-olefins, if originally formed in pyrogenetic processes, tend to rearrange

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[4] Egloff, "The Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1937, pp. 193–194.

[5] Tausz, *Chem. Z.*, **37**, 334 (1913); Tausz and von Putnoky, *Ber.*, **52B**, 1573 (1919).

mostly to β-olefins.[6] Hence, the following reaction seems to take place during the decomposition process

$$C_6H_{12}\text{ (Hexene-1)} \longrightarrow C_6H_{12}\text{ (Hexene-2)} \quad (4)$$

The formation of hexene-3 is also possible, but less likely.

The readings of refractive index of the products also check with the above assumption. A mixture of 70% of *n*-hexane and 30% of hexene-2 (or hexene-3) would have $n^{20}\text{D}$ about 1.382, while the value of the portion boiling between 66–70° before sulfuric acid treatment was 1.384. A mixture of hexene-1, which possesses a much lower $n^{20}\text{D}$, and *n*-hexane would give a far smaller value.[2]

The elucidation of the exact mechanism of the decomposition process requires further study. Owing to the present wartime pressure and difficulties, the investigation on this subject had to be discontinued.

[6] Brooks and Humphrey, This Journal, **40**, 832 (1918).

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Investigations on the Stereoisomerism of Unsaturated Compounds. VI. The Composition of Divinyl Glycol from Acrolein. The System *meso-dl*-Diethyl Glycol

By William G. Young, Stanley J. Cristol and Fred T. Weiss

It has been demonstrated conclusively that diastereomeric unsaturated glycols are formed in the pinacolic reduction of α,β-unsaturated aldehydes.[1,2,3,4] Young, Levanas and Jasaitis[3] have shown that, in the reduction of crotonaldehyde, *meso*- and *dl*-dipropenyl glycols, which may be hydrogenated to the corresponding dipropyl glycols, are formed in equal amounts as predicted on purely geometric grounds, but not found, by Kuhn and Rebel.[5] van Risseghem has prepared the diastereomeric diethyl glycols from acrolein by the similar reaction path

$$CH_2{=}CHCHO \xrightarrow[\text{HOAc}]{\text{Zn-Cu}}$$

$$\underset{\textit{meso-}\text{ and }\textit{dl-}\text{divinyl glycol}}{CH_2{=}CHCHOHCHOHCH{=}CH_2} \xrightarrow{H_2(Pt)}$$

$$\underset{\textit{meso-}\text{ and }\textit{dl-}\text{diethyl glycol}}{CH_3CH_2CHOHCHOHCH_2CH_3}$$

and has identified the individual isomers.

In the course of a study on the preparation of a number of pure stereoisomeric dibromides, we have prepared and separated the *dl*- and *meso*-diethyl glycols and have shown that the divinyl glycols are formed in equal quantities during the reduction of acrolein alone or in a mixture of acrolein and crotonaldehyde, contrary to the observations of Kuhn and Rebel.[5] This was accomplished by a determination of the melting point–composition diagram (Fig. 1) obtained by mixing the pure diastereomers, and by the use of this curve in a comparison with the melting point of the product mixture.

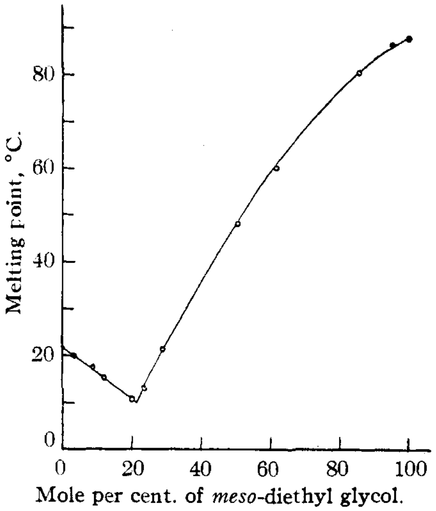

Fig. 1.—The melting point diagram of the system *meso*-, *dl*-diethyl glycol.

Experimental

Preparation and Separation of the Diethyl Glycols.—Divinyl glycol was prepared from acrolein by the method described previously[3] in the reduction of crotonaldehyde. The unsaturated glycol was hydrogenated with Adams platinum oxide catalyst[6] in 95% ethanol. After the catalyst was removed by centrifuging and the solvent removed by distillation, the melting point of the semi-solid residue was 50.4°. The solid was removed by filtration. Recrystallization from ligroin gave pure *meso*-diethyl glycol, m. p. 88.0–88.2°, m. p. of the bi-3,5-dinitrobenzoate, 190°.

The filtrate was fractionally distilled several times in a 3-foot long, adiabatic, metal spiral column at high reflux, until the lower boiling *dl*-isomer (b. p. 90.5–90.7° (8 mm.)) was obtained pure, m. p. 21.7°, m. p. of the bi-3,5-dinitrobenzoate, 167–168°. The melting point of this glycol did not increase upon redistillation or upon recrystallization from ligroin.

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[1] Farmer, Laroia, Switz and Thorpe, *J. Chem. Soc.*, 2937 (1927).

[2] Lespieau and Weimann, *Compt. rend.*, **194**, 1946 (1932); **195**, 886 (1933).

[3] Young, Levanas and Jasaitis, This Journal, **58**, 2274 (1936).

[4] van Risseghem, *Bull. soc. chim. Belg.*, **47**, 194 (1938).

[5] Kuhn and Rebel, *Ber.*, **60B**, 1565 (1927).

[6] Adams, Voorhees and Shriner, "Organic Syntheses," Vol. VIII, John Wiley and Sons, New York City, 1928, p. 92.