XXXIX.—*On the Products of the Oxidation of β Hexylic Alcohol.*

By J. A. WANKLYN and E. ERLLENMEYER.

WHEN β hexylic alcohol is oxidized with bichromate of potash and dilute sulphuric acid, it yields β hexylic aldehyde, according to the equation—

but, on pushing the action further, the next product is not caproic acid. Instead of simply taking up another atom of oxygen, the aldehyde falls in pieces when it is treated with more oxygen, and thus, in the second stage of oxidation, the products are butyric acid, water, and carbonic acid.

From this remarkable decomposition we see that two atoms of carbon in the β aldehyde and β alcohol are less firmly bound together than the remaining four carbon atoms. We might then express the difference between the β series and the ordinary or α series, by joining the carbon atoms differently in the two series.

We infer from this strange splitting up which the abnormal alcohol shows, that the difference between the normal and the abnormal series lies deeper than M. Wurtz seems to believe. In addition to β iodide, β alcohol, β aldehyde, and β ether, we think there is a β olefine and a β hydride.

We subjoin an account of β hexylic aldehyde, and of our experiments on the oxidation of β hexylic alcohol.

Preparation:—Bichromate of potash and dilute sulphuric acid are

heated in a retort, and β hexylic alcohol* is added by small portions at a time. The reaction is brisk, and an oily liquid of a sharp penetrating smell distils over. This distillate, which is the aldehyde, should be again distilled with bichromate of potash and dilute sulphuric acid. It may then be shaken up with aqueous solution of potash and dried with carbonate of potash.

Properties :— β $C_6H_{12}O$ has the penetrating fragrant smell which is characteristic of the aldehydes. It boils quite constantly at $127^\circ C$. (bar. = 761.2 mm.)

Its specific gravity at $0^\circ C$ = .8298

„ „ $50^\circ C$ = .7846

whence the expansion-coefficient for $50^\circ C$. = .0576.

It forms a solid compound with bisulphite of soda, and this compound is decomposed by boiling with water, the aldehyde being separated.

It does not reduce ammonio-nitrate of silver, and seems to have little or no tendency to take up oxygen from the air.

It is not easily (perhaps cannot be) transformed into an alcohol by the action of sodium-amalgam. The experiment was made in the presence of some ethylic alcohol, which would act as a solvent, but no transformation was effected.

Finally it is abnormal : for when oxidized it yields no caproic acid, but is broken up into carbonic acid, water, and butyric acid.

Analyses of it have furnished the following numbers :—

- I. .2956 grm. burnt with oxide of copper, a little chlorate of potassium being used, gave .7770 grm. CO_2 and .3229 grm. H_2O .
- II. .2896 grm. similarly treated gave .7608 grm. CO_2 and .3230 grm. H_2O .
- III. .2888 grm. similarly treated gave .7572 grm. CO_2 and .3184 grm. H_2O .

Calculated.		I.	Found.	III.
			II.	
C_6	72	71.69	71.65	71.51
H_{12}	12	12.14	12.39	12.25
O	16	—	—	—
	<hr/> 100			

* The β $C_6H_{14}O$ which we used was obtained from C_6H_{12} (prepared from mannite), by hydrating it by means of sulphuric acid. (See Chem. Soc. J., July, 1863.)

Notes of the experiments on the Oxidation of β C₆H₁₄O.

9.5 cub. cent. of β C₆H₁₄O were added by degrees to a heated mixture of 14 grms. bichromate of potash, 27 grms. sulphuric acid, and 20 grms. water. The reaction was very brisk, and a mixed distillate of oil and water came over. The distillate was shaken up with solution of potash, and the oily part (β C₆H₁₂O) put back into the retort and distilled over again along with the bichromate of potash, &c. This was repeated several times, and finally the distillate, supersaturated with potash, was evaporated in the water-bath. The concentrated residue was then distilled with sulphuric acid. The distillate was redistilled. It was then very acid, but free from sulphuric and hydrochloric acids. Ammonia was added to it and then solution of nitrate of silver, which determined an abundant white precipitate of silver-salt. The silver-salt having been washed, a small portion dried in the water-bath gave 56.73 per cent. of silver.

The rest of the silver-salt was then treated with dilute nitric acid and again washed. It was dried in the water-bath and analysed.

I. .1376 grm. gave on ignition .0775 grm. silver $\therefore$ silver % = 56.32.

II. .1516 grm. burnt with oxide of copper, a little chlorate of potash being used, gave .1323 grm. CO₂ and .0523 grm. H₂O.

This agrees with the composition of butyrate of silver:—

	Calculated.		Found.
C ₄	48	24.62	23.80
H ₇	7	3.59	3.83
Ag	108	55.38	56.32
O ₂	32	16.41	—
	<hr/> 195	<hr/> 100.00	

The theoretical percentage of silver in caproate of silver is 48.4 which is nearly 8 less than that which we find in our silver-salt. If the details which we have given be considered, it will be apparent that if any caproic acid had been formed at the beginning of the oxidation, we should have got hold of it; and inasmuch as caproate of silver is less soluble than its lower homologues, the prolonged

washing of the silver-salt should have favoured the accumulation of caproate in the latter portion of silver-salt whose analysis we have just given. The experiment was repeated.

7·5 grm. of bichromate
 15 cub. c. of sulphuric acid
 30 cub. c. of water
 3·5 cub. c. of hexylic alcohol

were taken. The oxidation soon stopped, when the oily distillate measured 2 cub. c., and it was necessary to take a fresh mixture of bichromate of potash, &c., in the same proportions as just given. An acid was finally obtained which was converted into a silver-salt—

·2206 grm. of the silver salt gave ·1237 grm. of silver.

Silver per cent. = 56·07, which confirms the result of the first experiment.

In a third experiment the formation of large quantities of carbonic acid during the oxidation was proved.

From all this we infer that when β $C_6H_{14}O$ is oxidized with bichromate of potash and dilute sulphuric acid, the first stage of the reaction is—

and the second—