

On the Electrolytic Reduction of Aldehydes, Part VII. Crotonaldehyde

By

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The electrolytic reduction of crotonaldehyde was first studied by Law¹ who reported that he obtained n-butyl alcohol with a yield of 70% by electrolysing an alcoholic sulphuric acid solution with a lead cathode. According to his communication, he used 25 grams of the aldehyde for reduction, and after passing a current of 2 amperes for 8 hours, fractionated the reduction product by distillation. He calculated the yield of the butyl alcohol simply by assuming that the portion distilled at temperatures up to 120° is n-butyl alcohol. Since the quantity of electricity he used was less than a half of the 38 ampere hours which theoretically are required for changing 25 grams of crotonaldehyde completely into butyl alcohol, it is quite inconceivable how he could have obtained the alcohol with such a high yield. There must be some errors in his calculation. With such a doubt in mind I traced Law's experiment exactly following his description, but could not get a better yield than 10%. Even when the reduction was cautiously performed by adding the aldehyde drop by drop to the cathode solution in the course of electrolysis and keeping the temperature at 0°—5°, the yield could not be raised higher than 50%.

As it was thus made clear that the electrolytic reduction of crotonaldehyde can not be brought about so easily as Law states, a further investigation of this problem was deemed not to be superfluous.

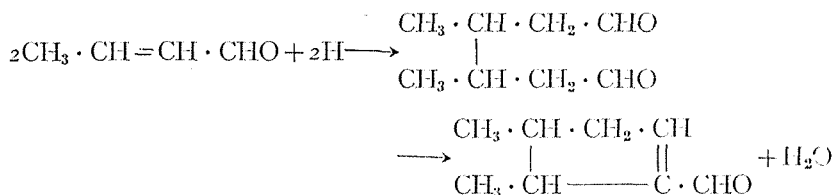
In the previous communication² I reported that the carbonyl group

¹ J. Chem. Soc., **101**, 1016 (1912).

² These Memoirs, **12**, 327 (1929).

in α , β -unsaturated ketone is reducible only with great difficulty and consequently the action of reduction is solely directed towards the double bond. Now α , β -unsaturated aldehyde behaves somewhat differently, the reduction of its carbonyl and of its ethylene group taking place side by side and producing n-butyl aldehyde, crotonyl alcohol and n-butyl alcohol, together with a pinacone and pinacolone. Of these reduction-products pinacone was always found as the chief product, and the yield of n-butyl alcohol could not be raised more than 50% in spite of all efforts.

Hibbert and Read¹ reported that they obtained dimethyl-cyclopentene aldehyde on electrolysing dilute sulphuric and acetic acid solutions of crotonaldehyde with a lead or zinc electrode, and explained its formation in the following way:



This conclusion was drawn from the results of analysis and the molecular weight determination of the final product and its semicarbazone on the one hand, and on the other hand from the analogy that several cyclocompounds are produced from diacetylbutane², dihydroxysuberic acid³ and mesityl oxide⁴. It is here to be noted that the reduction product of mesityl oxide which Harries and Hübner had regarded as pentamethyl cyclopentene was afterwards confirmed by Law's experiment⁵ to be nothing but a pinacolone.

The evidence on which the reduction-product of crotonaldehyde was assumed to be methyl cyclopentene aldehyde having been deemed still insufficient, I repeated Hibbert and Read's experiment, and, instead of directly distilling with steam as the American chemists did, subjected the reduction-product to fractional distillation under reduced pressure, and a colourless viscous oil was isolated as a portion boiling at 123°—

1 J. Am. Chem. Soc., **46**, 989 (1924).

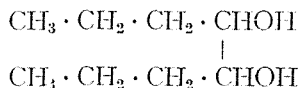
2 Marshall and Perkin, J. Chem. Soc., **57**, 204 (1890); **57**, 241 (1890).

3 Baeyer and von Liebig, Ber., **31**, 2106 (1898).

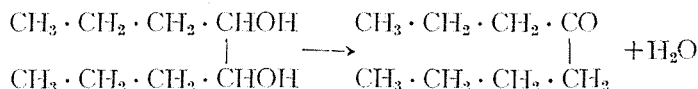
4 Harries and Hübner, Ann., **296**, 295 (1897).

5 J. Chem. Soc., **101**, 1016 (1912).

125° under 5 mm pressure. It gave no semicarbazone, and the results of analysis and the molecular weight determination showed it to be a pinacone of the formula,



When it was mixed with some dilute sulphuric acid and distilled with steam, an aromatic oil resembling menthol in its odour was distilled, and a brown resinous matter was left as the residue. After the oil had been repeatedly fractionated, the portion distilling between 165° and 168° was collected and examined. It easily changed to the semicarbazone melting at 185°–186°, and its molecular weight as well as the result of analysis well agreed with the value found by Hibbert and Read. It was not, however, dimethyl cyclopentene aldehyde as they supposed, but an octanone formed from the pinacone by dehydration, thus:



Experimental

I. Electrolytic reduction in a faintly acidic solution

A cathode solution made faintly acidic with acetic acid was first used.

Cathode solution: 20 grams crotonaldehyde + 50 c.c. alcohol + 50 c.c. water + 5 c.c. glacial acetic acid + 10 grams sodium acetate.

Anode solution: 10% caustic soda solution.

Cathode: Mercury (50 sq. cm.); Anode: Platinum plate.

Current strength: 4 amperes; Temp.: 30°–40°.

During the electrolysis, acetic acid was added to the cathode solution to keep it always in an acidic state. After 5 hours' electrolysis the cathode solution was diluted with water and well shaken with ether. The ether extract was then distilled under 5 mm. pressure and the portion boiling up to 120° (6–7 grams) and that distilling at 120°–130° (8–10 grams) were collected. Besides these, about 2 grams of

a substance having a higher boiling point was also obtained.

When the portion distilled at temperatures lower than 120° under 5 mm. pressure was subjected to fractional distillation under ordinary pressure, about 2—3 grams of n-butyl alcohol mixed with a small quantity of unsaturated alcohol, perhaps crotonyl alcohol, was obtained as the portion boiling at 110° — 125° . As it was found difficult to collect the distillate of definite higher boiling point by continuing the distillation under ordinary pressure, the further fractionation was conducted under 10 mm. pressure, and octadiene(2,6)diol(4,5) $\text{CH}_3 \cdot \text{CH} = \text{CH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CH} = \text{CH} \cdot \text{CH}_3$ was isolated as a colourless oil distilling at 120° — 125° . It decolourized bromine and produced no semicarbazone. The result of analysis was as follows:

0.1327 gm. substance gave 0.3261 gm. CO_2 + 0.1182 gm. H_2O ,
C=67.01%, H=9.97% (Calc. C=67.56%, H=9.93%).

Its molecular weight was determined by the cryoscopic method benzene being used as the solvent, and the values 159.3 and 161.4 were obtained for the theoretical value, 142.1.

From the fraction distilled at 120° — 130° under 5 mm. pressure a colourless viscous oil with an agreeable odour was separated. It boiled at 123° — 125° under 5 mm. pressure and yielded neither the hydrazone nor semicarbazone. The results of elementary analysis and molecular weight determination described below showed it to be octanediol¹.

0.1827 gm. substance gave 0.4460 gm. CO_2 + 0.1798 gm. H_2O ,
C=65.15%, H=11.80% (Calc. C=65.67%, H=12.41%).

Substance taken	Benzene	Dep. of F. P.	Mol. Wt.	
gm.	gm.	$^{\circ}\text{C}$	Found	Calc.
0.1613	26.47	0.19	162	
0.1104	21.41	0.17	153	146

When the distillate distilled at 120° — 130° under 5 mm. pressure, with some dilute sulphuric acid added, was subjected to steam distillation, an ethereal oil having an odour resembling that of menthol was obtained. The purified sample boiling at 165° — 168° was analysed.

0.1522 gm. substance gave 0.4209 gm. CO_2 + 0.1447 gm. H_2O ,
C=75.42%, H=10.64% (Calc. for octanone, $\text{C}_8\text{H}_{16}\text{O}$, C=76.14%,
H=11.19%).

The molecular weight determination also gave a result which

¹ Bouveault and Locquin, C. r., **140**, 1699; Bl (2) **35**, 644, 647 (1905).

showed it to be octanone, as follows :

Substance taken	Benzene	Dep. of F. P.	Mol. Wt.	
gm.	gm.	°C.	Found	Calc.
0.1509	22.15	0.27	129	
0.2935	,,	0.51	133	
0.4309	,,	0.74	135	132

Thus the substance is evidently octanone(4), $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$, which was once prepared by Bouveault and Locquin¹ by heating octanediol(4,5) with dilute sulphuric acid in a sealed tube at about 200°. It easily changed to the semicarbazone crystallising in white needles and melting at 185°—186°. The nitrogen content was determined by Kjeldahl's method, thus :

0.1540 gm. substance produced ammonia which required 30.64 c.c. of 0.0786 N-HCl for neutralization.

$$N = 21.9\% \text{ (Calc. for } \text{C}_9\text{H}_{19}\text{ON}_3, N = 22.7\%).$$

II. *Electrolytic reduction in a sulphuric acid solution*

The reduction experiment was conducted under the following conditions :

Cathode solution : 100 c.c. 2N—H₂SO₄ + 20 gm. crotonaldehyde.

Cathode : Lead plate (90 sq. cm.).

Anode solution : 2N—H₂SO₄

Anode : Lead ; Temperature : 30—40°

Current strength : 3 amperes ; Time : 6 hours.

After electrolysis the cathode solution was neutralised and distilled with steam, and the oil thus obtained was fractionated into three parts.

- 1) First fraction distilled at temperatures up to 110° 1 gm.
- 2) Second " " " at 110°—125° 0.5 gm.
- 3) Third " " " at 165°—175° 3 gm.

The yield of the second portion, chiefly consisting of n-butyl alcohol, was thus seen to amount to not more than 3%. The third fraction was found to consist of octanone-(4) previously described.

Another experiment was finally carried out exactly under the conditions adopted by Law.²

¹ Loc. cit.

² Loc. cit.

Cathode solution : 50 c.c. alcohol + 150 c.c. H_2O + 10 gm. H_2SO_4 + 20 gm. crotonaldehyde.

Cathode : Lead (90 sq. cm)

Current strength : 3 amperes ; Time : 6 hours,

When the electrolysis was over, the cathode solution was extracted with ether, and the ether extract was fractionated with distillation under ordinary pressure. The quantities of the various fractions varied according to the temperatures used for the electrolysis thus :

Temp.	Distillate up to 110° Butylaldehyde Crotonaldehyde	Distillate at 110°—125° Butylalcohol Crotonylalcohol	Distillate at 125°—240° Pinacone etc.	Residue
0°—5°	30%	8%	50%	5%
10°—15°	21 „	5 „	55 „	10 „
20°—25°	20 „	3 „	45 „	25 „

The greater portion of the first fraction distilled at temperatures lower than 90°, and the distillate easily formed nitrophenylhydrazone crystallizing in beautiful orange needles. The hydrazone was soluble in alcohol, benzene and toluene, but with difficulty in ligroin and water. It melted at 93°—95°. After being reduced with zinc and salicylic acid it was analysed by Kjeldahl's method.

0.1668 gm. substance gave ammonia which required 31.82 c.c. of 0.0786 N-HCl for neutralization.

$$N = 20.99\% \text{ (Calc. for } C_{10}H_{13}N_3O_2, N = 20.27\%)$$

As is seen from the above results, n-butyl alcohol could not be produced from crotonaldehyde with such a high yield as Law states. It was found, however, that the yield could be increased to 50%, if we took a dilute sulphuric acid solution of about 2.5%, to which no alcohol had been added, as the cathode solution and electrolysed it at 0°—5° adding crotonaldehyde little by little to the cathode solution in the course of the electrolysis. The use of a lead cathode in a 25% acetic acid solution, and a mercury cathode in a sodium bicarbonate solution were found equally effective.

The writer takes this opportunity warmly to thank Professor M. Matsui under whose kind guidance this investigation was carried out.