

resultant opening of the pyrrolidone ring, the carboxyl group is again active. The reason for the loss of acidic properties with the closed pyrrolidone ring is the formation of a six-membered ring between the terminal carboxyl and the carbonyl group on Carbon 2.

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THE ELECTROLYTIC REDUCTION OF ACROLEIN^{1,2}

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The reduction, by electrochemical means of α,β -unsaturated aliphatic aldehydes has been investigated to only a slight extent. According to Law³ the electro-reduction of crotonaldehyde yields only butyl alcohol. On the other hand, Hibbert and Read,⁴ using very similar conditions, showed that the same aldehyde yielded not only butyl alcohol and butyraldehyde but also a new product, dimethyl-cyclopentene aldehyde.

The appearance of dimethyl-cyclopentene aldehyde during the reduction of crotonaldehyde was quite unexpected, and the structure ascribed to it was later confirmed⁵ by its direct synthesis from β -bromobutyraldehyde diethyl acetal.

It seemed advisable, in view of the desirability of settling definitely the course of the reaction leading to the formation of the dimethyl-cyclopentene aldehyde, to study the reduction of another member of the same series. Acrolein was, therefore, chosen, inasmuch as all of the possible reduction products, that is, propionaldehyde, propyl alcohol, allyl alcohol, dipropenyl glycol and cyclopentene aldehyde,⁶ have been identified.⁷

A discussion of the nature of the chemical reduction of crotonaldehyde has been given in a previous paper,⁴ the amounts of the various products formed, that is, butyraldehyde, crotyl alcohol, butyl alcohol and dipropenyl glycol, varying with the conditions and reagent employed. On the other hand, the electrochemical reduction of this aldehyde did not yield

¹ Communicated to the Organic Division, American Chemical Society, Baltimore, Maryland, April, 1924.

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³ Law, *J. Chem. Soc.*, **101**, 1016 (1912).

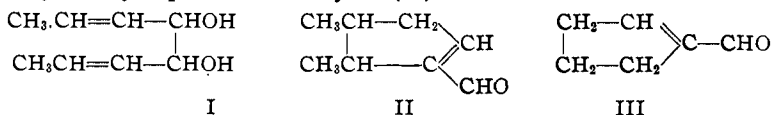
⁴ Hibbert and Read, *THIS JOURNAL*, **46**, 983 (1924).

⁵ Read and Hibbert, *ibid.*, **46**, 1281 (1924).

⁶ As the semicarbazone, Baeyer and von Liebig, *Ber.*, **31**, 2106 (1898). The aldehyde has not been isolated heretofore.

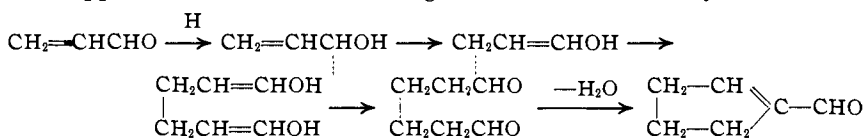
⁷ Linnemann, *Ann. (Supp.)*, **III**, 257 (1864-65). Griner, *Ann. chim. phys.*, [6] **26**, 368 (1892). Sabatier, *ibid.*, [8] **4**, 398 (1905). Harries, *Ann.*, **330**, 226 (1903). Skita, *Ber.*, **45**, 3312 (1912).

dipropenyl glycol (I) but an unsaturated cyclic aldehyde, namely, 4,5-dimethyl- Δ' -cyclopentene aldehyde (II).



If the electro-reduction of acrolein proceeds in an analogous manner, the products formed should be propionaldehyde, propyl alcohol and the corresponding cyclopentene aldehyde (III); and their formation would thus provide considerable support for the previous views put forward relative to the course of the reduction of crotonaldehyde.

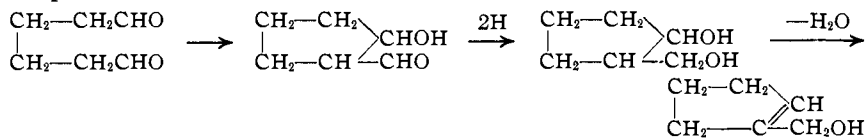
As applied to acrolein the following course of reduction may be assumed.



It was found possible to separate and identify the cyclopentene aldehyde, and while the yield of the cyclic aldehyde was not high, in view of the activity of the intermediate and final products, it may be considered satisfactory. A quantity of high-boiling, unidentifiable residue was always obtained.

It is to be expected that the new compound, as an α,β -unsaturated aldehyde, should be readily reducible under conditions similar to those under which it is formed and this was found to be the case although it was not found possible to isolate any definite substance from the mixture formed.

If the theoretical explanation previously put forward⁸ for the course of the reduction is correct, it follows that an aldol condensation product should be formed intermediate between the hexanedial and cyclopentene aldehyde; such a hydroxy aldehyde should be readily reducible under the existing conditions.⁹ The fact that it was actually possible to isolate a small amount of a compound apparently possessing the structure of Δ' -cyclopentene carbinol lends added weight to the views previously adopted.



The small quantity obtained rendered a satisfactory isolation and purification difficult.

⁸ Ref. 4, p. 990.

⁹ Ref. 4. See reference to acetaldo and diacetone alcohol.

Experimental Part

The apparatus and manipulation of the electro-reduction was identical with those employed by Read and Hibbert.⁴ The results of several typical reductions are given in Table I.

TABLE I
REDUCTION DATA

40 g. of acrolein was added in each instance; the current was 3 amperes.

Run	Duration of run hrs.; min.	Hydrogen from coulomb-meter, liters	Hydrogen from reduction cell, liters	Hydrogen absorbed	Hydrogen absorbed per mole of acrolein		Potential drop, volts	Temp., °C.
					liters	Equivalents per mole		
1	6:10	8.10	0.45	7.65	10.92	0.95	0.55	0
2	4:50	7.35	.58	6.73	9.49	.83	.64	15
3	5:25	7.95	.70	7.25	10.15	.88	.58	12
4	6:15	8.90	.22	8.68	12.15	1.05	.71	12
5	6:3557	0

In every case the catholyte at the end of the reduction still retained the strong odor of acrolein. It may be noted, however, that only very small amounts of acrolein are needed to produce such an odor.

The maximum yield of cyclopentene aldehyde was obtained when the crude acid-reduction product was made up to a sulfuric acid content of 5% and then heated to a temperature of about 90°. At this point the solution became cloudy and finally deep yellow. The heating was then stopped, the solution cooled to 0° and extracted with ether. It was then saturated with sodium chloride and again extracted. The combined ether extracts were dried over anhydrous sodium sulfate, the ether was removed and the residue fractionated through a bead column 4 to 5 cm. long.

The fractions obtained are shown in Table II.

TABLE II
PRODUCTS OF REDUCTION

B. p., °C.	Description	Yield, %	Remarks
(a) 34- 40	Ether and acrolein		Discarded
(b) 40- 80	Acrolein and propionaldehyde	6	
(c) 85-100	Allyl and propyl alcohols	9	
(d) 100-145			Rapid rise in temperature
(e) 145-155	Cyclopentene aldehyde (crude)	20	B. p. 149-150°
(f) 155-165	Containing cyclopentene carbinol		B. p. 162-165°

The cyclopentene aldehyde obtained in the first distillation boiled between 140° and 160°, and yielded, on re-distillation, a product possessing a typical aldehyde odor; b. p., 149-150°.

Water was observed in the distillate passing over between 85° and 145°. Since the ether extract was carefully dried before distillation, this would indicate the formation of an intermediate reduction product, which by the

loss of water gives rise to the formation of cyclopentene aldehyde, according to the theory already stated.

Each of the above-mentioned fractions (b-f) was treated separately with anhydrous sodium sulfate to remove water and then redistilled.

Cyclopentene Aldehyde.—Analysis for carbon and hydrogen was unsatisfactory, due probably, as was the case with dimethyl-cyclopentene aldehyde, to the presence of either hexanedial or its condensation product. It gave the usual aldehyde reactions, and titration with bromine in carbon tetrachloride showed the presence of one double bond; b. p., 159–160°.

Anal. Subs., 0.1307: Br, 0.0812. Calcd. for one double bond: 62.5%. Found: 62.1%.

Mol. wt. Subs., 0.0893: benzene, 8.44; Δt , 0.490°. Calcd. for C_5H_8O : mol. wt., 96. Found: 108.

Identification of Cyclopentene Aldehyde Derivatives.— Δ' -Cyclopentene aldehyde semicarbazone was prepared by the usual procedure. A precipitate formed at once and after standing for one hour it was filtered off by suction, washed with cold water and dried. It was soluble in hot water, from which it was recrystallized three times. It was found that a boiling solution of the semicarbazone decomposed slightly. The observed melting point was the same as that found by Baeyer and von Liebig;⁶ m. p., 208° (corr.). The crystals of cyclopentene aldehyde semicarbazone were found to be optically biaxial, either monoclinic or orthorhombic, stout rectangular prisms. Examination of crystals obtained from different samples showed them to be identical.

Δ' -CYCLOPENTENE CARBOXYLIC ACID.—This was prepared by oxidizing the aldehyde with silver oxide. The cyclopentene carboxylic acid formed was recrystallized from hot water in the form of long needles and then sublimed; m. p., 120° (corr.). This melting point was not changed by a second sublimation and is that given previously for this compound.¹⁰

Δ' -CYCLOPENTENE- β -NAPHTHOCINCHONINIC ACID.—This derivative of cyclopentene aldehyde was prepared according to the directions given by Doebner.¹¹ The product was recrystallized from alcohol, forming needle-shaped, brown crystals; m. p., 241–243° (corr.). The melting point was not changed by a second crystallization.

Anal. Subs., 0.1168 g.: 4.25 cc. of 0.0904 *N* HCl. Calcd. for $C_{19}H_{16}NO_2$: N, 4.8. Found: 4.6.

Δ' -CYCLOPENTENE CARBINOL.—A careful re-fractionation of the product which boiled at 155–165°, obtained from several runs, yielded a liquid boiling at 162–165°. This contained one double bond and an hydroxy group.

Anal. Subs., 0.1870 g.: CO_2 , 0.4952; H_2O , 0.1525. Calcd. for $C_6H_{10}O$: C, 73.4; H, 10.2. Found: C, 72.3; H, 9.6.

¹⁰ *J. Chem. Soc.*, 65, 101 (1897). *Ber.*, 31, 2108 (1898).

¹¹ *Ber.*, 27, 352 (1894).

BEHAVIOR OF DIVINYL GLYCOL.—Two hundred g. of acrolein dissolved in one liter of water was treated during 96 hours with 150 g. of zinc copper couple,¹² 300 g. of acetic acid being added during the first 48 hours. The resulting product was treated with dry sodium carbonate, filtered and sufficient sodium hydroxide solution added to complete the neutralization. After filtration, the product was extracted with ether, the solution then saturated with potassium carbonate and further extracted. The combined ether extracts after drying over sodium sulfate yielded 68 g. (29%) of divinyl glycol; m. p., 97–104° (16 mm.). Forty-five g. of this glycol dissolved in 400 g. of 2% sulfuric acid was allowed to stand for two hours at 15° in contact with strips of lead. The product was then worked up as though it had resulted from a reduction. No product other than divinyl glycol could be isolated. The aqueous solution left after the extraction was steam distilled and the distillate extracted with ether. No product other than a trace of divinyl glycol was found.

Summary

1. Acrolein readily undergoes reduction in dil. sulfuric acid, lead electrodes being used, and the products formed are propionaldehyde, allyl and propyl alcohols, Δ' -cyclopentene aldehyde and probably traces of Δ' -cyclopentene carbinol.

2. Divinyl glycol under similar conditions does not undergo rearrangement to give any product resembling Δ' -cyclopentene aldehyde.

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THE ACTION OF ALKYL CHLOROCARBONATES ON HYDROXY-ARYLARSONIC ACIDS

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Recently, in making a study of the action of alkyl chlorocarbonates on amino-arylarsonic acids, it was shown that in the case of 3-amino-4-hydroxy-phenylarsonic acids, both the amino- and the hydroxyl- groups reacted with the chlorocarbonates.¹

In this work the action of alkyl chlorocarbonates on hydroxy-aryl- arsonic acids was investigated more fully. Methyl, ethyl, propyl, *iso*-propyl, butyl and *isobutyl* chlorocarbonates were condensed with *p*-hydroxy-phenylarsonic acid, *m*-hydroxy-phenylarsonic acid and 3-nitro-4-hydroxy-phenylarsonic acid. This was accomplished by adding the alkyl

¹² Prepared by washing 80-mesh zinc dust thrice with a dilute copper sulfate solution sufficient to cover the zinc, and finally washing with water.

¹ Hamilton and Sly, *THIS JOURNAL*, **47**, 435 (1925).