At any rate, a simple aliphatic derivative, such as *n*-hexylchloromalonamide, with a sweetening power of 300, is something of a novelty. This substance has the disadvantage, however, of difficult solubility in water.

Summary

In a series of alkylchloromalonamides, with alkyl varying in size from methyl to hexyl, all the normal derivatives were found to have a decidedly sweet taste. The *n*-butyl derivative was both bitter and sweet. With branched-chain alkyls, such as *iso*butyl and *iso*-amyl, bitterness predominated and entirely masked any evidence of sweetness. The maximum sweetness was reached with the *n*-hexyl derivative of which 1 part in 5000 of water had the sweetness of a 6% sucrose solution. Most remarkable is the fact that the next lower homolog, *iso*-amylchloromalonamide, which differs by one carbon and a branching of the chain, is intensely bitter. No constant variation in sweetness could be established in this series.

DETROIT, MICHIGAN

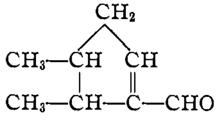
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

STUDIES ON THE REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. IX. SYNTHESIS OF 2,3-DIMETHYL-CYCLOPENTENE ALDEHYDE[1]

BY ROLAND R. READ AND HAROLD HIBBERT

RECEIVED FEBRUARY 9, 1924

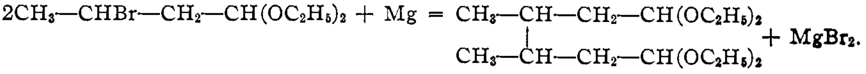
In the previous communication (Part VIII) it was shown that crotonaldehyde on electrolytic reduction yields an unsaturated aldehyde to which the following structure was assigned,



namely, 2,3 dimethyl-cyclopentene aldehyde.

In view of the unusual course of this reaction, it was considered advisable to establish, definitely, the structure of the product by direct synthesis, and this has been effected in the following manner:

β-Bromobutyraldehyde diethyl acetal, on treatment with magnesium in ether solution, is converted into the diethyl acetal of adipic aldehyde.



$$2CH_3—CHBr—CH_2—CH(OC_2H_5)_2 + Mg = \begin{array}{l} CH_3—CH—CH_2—CH(OC_2H_5)_2 \\ \quad\quad\;\, | \\ CH_3—CH—CH_2—CH(OC_2H_5)_2 \end{array} + MgBr_2.$$

This, on hydrolysis with dil. sulfuric acid, yields 2,3-dimethyl-cyclo-

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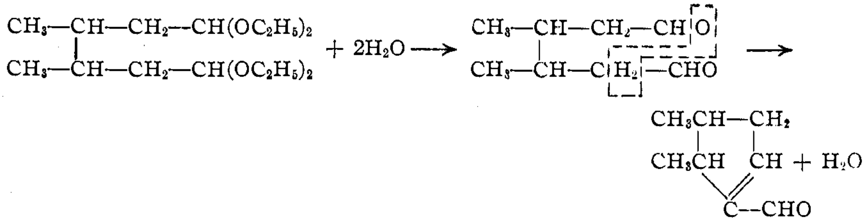
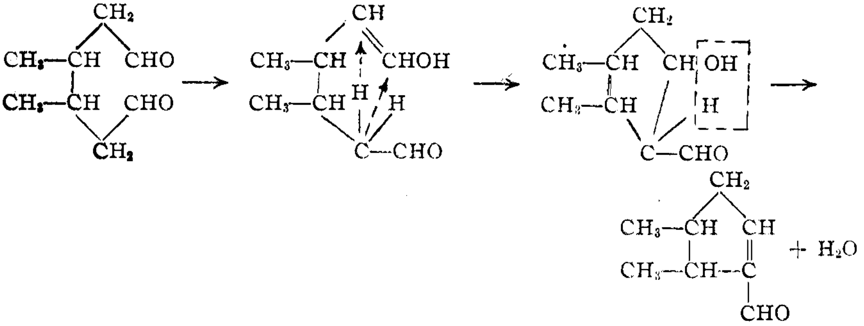
[1] This work was carried out at the University of Vermont.

pentene aldehyde, the dimethyl-adipic aldehyde first formed then losing water under the influence of the dilute acid.[2]



It is possible that we are dealing here with a type of intramolecular aldol "formation," followed by "crotonization."



Experimental Part

Preparation of β-Bromobutyraldehyde Diethyl Acetal, $CH_3CHBr\text{-}CH_2CH(OC_2H_5)_2$.—A current of dry hydrogen bromide (prepared catalytically by passing a mixture of hydrogen and dry bromine vapor over a heated platinum spiral) was passed into 50 g. of absolute ethyl alcohol, maintained at 0°, until the increase in weight amounted to 45 g. To this solution, vigorously stirred, 25 g. of crotonaldehyde was added, the temperature being maintained below 5°. After agitating this product for 15 minutes, the acetal soon separated as a heavy, yellow oil. This was removed, diluted with 10 cc. of absolute alcohol, and while the solution was stirred, dry calcium carbonate (about 5 g.) was gradually added until effervescence ceased, the temperature being kept below 10°. The product was mixed with 25 cc. of water, whereupon a further evolution of carbon dioxide occurred, some of the calcium carbonate being left undissolved. After filtration of the mixture, the crude acetal was freed from alcohol by shaking it thrice with a concentrated solution of calcium chloride, and once with water; then it was dried with potassium carbonate and distilled; yield, 40 g. (80%); b. p., 82–85° (12–15 mm.).

The product is unstable, and darkens in color rapidly; it becomes acid to litmus, and acquires an odor of crotonaldehyde. It cannot be distilled unchanged, even under diminished pressure, in larger quantities than about 50 g., while at ordinary pressure there is practically complete decomposition.

Analysis. Subs., 0.1309: AgBr, 0.1051. Calc. for $C_8H_{17}O_2Br$: Br, 35.4. Found: 34.2.

The low value is due to the difficulties involved in isolating a pure product.

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[2] This property appears to be characteristic of such aldehydes. Wohl and Schweitzer, *Ber.*, **39**, 894 (1906).

Conversion of the Acetal to 2,3-Dimethyl-cyclopentene Aldehyde.—Five g. of magnesium turnings was added during the course of four hours to 50 g. of the bromo-acetal dissolved in 75 g. of ether, the temperature being maintained so that continual refluxing occurred. After this mixture had been heated for another four hours, and then cooled, sufficient water was added to decompose the thick, pasty, lower layer, and then about 15 cc. of sulfuric acid (1:1) until the solution was distinctly acid. The ether was removed, the aqueous solution refluxed for two hours, the product distilled with steam and the distillate extracted with ether. The ether solution was dried over calcium chloride and fractionated, yielding 2.6 g. (20%) of an oil boiling between 160° and 170°, which possessed the pungent odor of 2,3-dimethyl-cyclopentene aldehyde. This corresponded in all of its properties with the product obtained by the electrolytic reduction of crotonaldehyde.[3] The semicarbazone melted at the same temperature (184–186°) and a mixture of the two produced no alteration in the melting point.

Analysis of the semicarbazone. Subs., 0.1267: 26.1 cc. of N_2 (over water, 19°, 747 mm.). Calc. for $C_9H_{15}ON_3$: N, 23.2. Found: 23.4.

The attempt to substitute the corresponding chlorobutyraldehyde diethyl acetal[4] for the bromo derivative in the above reaction was not successful.

Summary

2,3-Dimethyl-cyclopentene aldehyde has been synthesized and shown to be identical with the unsaturated aldehyde obtained by the electrolytic reduction of crotonaldehyde.

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[Contribution from the Department of Chemistry, Yale University]

STUDIES ON THE REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

X. SYNTHESIS AND RELATIVE STABILITY OF CYCLIC ACETALS FROM 1,2- AND 1,3-GLYCOLS

By Harold Hibbert and John Arrend Timm[1,2]

Received February 9, 1924

In a previous communication[3] it was shown that on treating a mixture of one molecular equivalent each of a 1,2- and a 1,3-glycol with one equivalent of acetylene in the presence of small amounts of sulfuric acid and a mercury salt as catalyst, a partition of the acetylene takes place resulting in the formation of a mixture of cyclic acetals, namely, of a 5- and a 6-membered derivative, the latter always in the larger amount.

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[3] Part VIII. This Journal, **46**, 997 (1924).

[4] Wohl and Frank, *Ber.*, **35**, 1905 (1902).

[1] This paper is constructed from Part I of a dissertation presented by John Arrend Timm in June, 1922, to the Faculty of the Graduate School of Yale University, in candidacy for the degree of Doctor of Philosophy. The thesis contains a review of the literature on cyclic acetal formation.

[2] Communicated to the Cellulose Section, American Chemical Society, Birmingham, Alabama, April, 1922.

[3] This Journal, **45**, 3117 (1923).