cating in one case a high percentage of alkylation and in the other a large amount of extraction of hydrogen to form ethane, the reactions in both cases being accompanied by the conversion of very large percentages of the original hydrocarbons to both higher olefin and paraffin compounds.

In order to give some idea of the possible length of the reaction chains, the relation of the amount of polymerized ethylene to the theoretical amount of ethyl radicals is presented in Table I. This is very well shown in run 14, in which the amount of ethylene in respect to the amount of tetraethyllead was quite large. This fact as well as the apparent molecular size of the liquid reaction products supports the assumption that large radicals are formed as postulated by Taylor and Jones.[1]

In conclusion the writer wishes to thank T. A. Boyd for his interest in this work and for his aid in the preparation of the manuscript.

Summary

A study has been made of the thermal decomposition of tetraethyllead in solution in benzene and also in benzene with varying amounts of ethylene and hydrogen.

Evidence has been presented in favor of the assumption that the predominating reaction of ethyl radicals in solution is that of disproportionation and that the ethylene so formed is converted to higher hydrocarbons as induced by ethyl radicals.

Evidence has been presented to show that molecular hydrogen takes part in this type of reaction to only a small extent, if any.

Large amounts of ethylene are converted to light colored oils by the simultaneous decomposition of tetraethyllead. Evidence has been presented in support of the assumptions, made by previous investigators, that these reactions are induced by ethyl radicals.

DETROIT, MICHIGAN RECEIVED FEBRUARY 15, 1934

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Occurrence of Citral in Florida Valencia Orange Oil[1]

BY E. K. NELSON AND H. H. MOTTERN

Florida Valencia orange oil was prepared in the United States Citrus Products Laboratory at Winter Haven, Florida, by pressing the peel in a Pipkin oil machine and centrifuging the expressed liquid. The amount of oil available (2710 g.) was insufficient for a complete examination because, after removal of the limonene by direct distillation at 10 mm., and distillation of the residue with steam, but 92 g. of terpene-less oil was obtained.

This oil was examined for aldehydes, particular attention being paid to the possible presence of citral. For the separation of aldehydes, the method of Tiemann[2] was used because by the ordinary method of shaking with a solution of sodium bisulfite the citral may go into solution as the stable dihydrodisulfonic acid derivative, from which it cannot be recovered.

The oil was shaken for six hours with a solution of 26 g. of sodium sulfite and 30 g. of sodium bicarbonate in 350 cc. of water. After standing overnight in the refrigerator, the crystalline bisulfite compound was separated by filtration.

A solution of 15 g. of sodium hydroxide was added to the filtrate, and the separated oil, which had a pronounced odor of citral, was extracted with ether. Careful evaporation of the ether gave 3.8 g. of aldehyde which had gone into solution as the labile dihydrodisulfonic acid derivative.

The semicarbazone was prepared and extracted with ether to remove β-citral semicarbazone. Recrystallized several times it melted at 160–162°, and optical crystallographic comparison[3] with α-citral semicarbazone showed its identity with that substance. The α-citryl β-naphthocinchoninic acid was also prepared. It melted at 206°, and a mixture with the same derivative prepared from pure citral gave no depression in melting point.

From the crystalline bisulfite compound, 6.1 g. of aldehyde was recovered.

The main fraction of this boiled at 90–92° at 10 mm., melted at 17–18°, and gave an oxime melting at 65–67°. It is therefore decyl aldehyde.

Decyl aldehyde has been found in orange oil

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[1] Food Research Division Contribution No. 212.

[2] Tiemann, *Ber.*, **31**, 3318–3320 (1898).

[3] Optical crystallographic examination was made by G. L. Keenan, Food and Drug Administration.

by K. Stephan[4] and in California orange oil by Poore.[5]

Semmler[6] reported the presence of citral in orange oil, but Gildemeister and Hoffmann[7] state that Semmler's orange oil must surely have been adulterated with lemon oil. This criticism, however, cannot apply to our material, as no lemons had been pressed in the machine used and the oil was an authentic sample, expressed by one of us in Florida.

The probability is that citral has previously been overlooked in the examination of orange oils as it is sure to escape notice if it goes into solution as the stable dihydrodisulfonic acid derivative.

Summary

Decyl aldehyde and citral have been shown to be aldehydes present in Florida Valencia orange oil.

WASHINGTON, D. C. RECEIVED FEBRUARY 19, 1934

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[4] Stephan, *J. prakt. Chem.*, [II] **62**, 523 (1900).

[5] Poore Tech. Bull. 241, U. S. Dept. Agr., 1932.

[6] Semmler, *Ber.*, **24**, 202 (1891).

[7] Gildemeister and Hoffmann, "Die Oetherischen Oele," 3d ed., 1931, Vol. III, p. 83.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Studies of Conjugated Systems. XV. The Addition of Hydrogen Chloride to the Geometric Isomers of Phenylbutadiene

BY IRVING E. MUSKAT AND K. A. HUGGINS

Riiber[1] studied the addition of hydrogen bromide to phenylbutadiene. After considerable experimentation he found he was unable to isolate a definite mono-hydrogen bromide addition product. He did isolate, however, a crystalline product, m. p. 146°, to which he assigned the formula $C_{10}H_9Br\cdot 2HBr$. He further treated this compound with dimethyl zinc and obtained a hydrocarbon $C_{11}H_{14}$. He studied the oxidation of this product and concluded that the hydrogen bromide was absorbed in the 3,4-positions of 1-phenylbutadiene.

For the development of our theory on the addition reactions of conjugated systems, we had to be certain of the mode of additon of the halogen acids to conjugated compounds. We therefore decided to study the addition of hydrogen chloride to phenylbutadiene, our aim being to isolate a pure mono-hydrogen chloride addition compound and determine its structure.

The addition of hydrogen chloride to *trans*-phenylbutadiene was first studied. It was found that *trans*-phenylbutadiene absorbed one mole of hydrogen chloride to form a slightly yellow oil which distilled at 103° under 5 mm. pressure. An almost quantitative yield of this product was obtained.

The structure of this hydrogen chloride addition product was determined by ozonization. It was possible to isolate from the ozonization products a 72.8% yield of benzaldehyde as calculated from its semicarbazone and the benzoic acid that was recovered. This proves that hydrogen chloride adds to *trans*-phenylbutadiene in the 3,4-positions.

This hydrogen chloride addition product is identical with the product prepared by Muskat and Herrman[2] from the *trans*-1-phenyl-3-hydroxy-Δ^1-butene. Consequently the hydrogen chloride addition product must have the structure *trans*-1-phenyl-3-chloro-Δ^1-butene.

The addition of hydrogen chloride to *cis*-phenylbutadiene was then studied. An unstable addition product was obtained which distilled at 106° under 5 mm. pressure. The chloride was so unstable that it lost hydrogen chloride on standing, and it was not possible to obtain an absolutely pure compound. A number of attempts were made to prepare a pure sample of the chloride by varying the temperature and solvent but the results were all the same. The best analytical data obtained were 1% low in chlorine.

The structure of the hydrogen chloride addition product was determined by ozonization. It was possible to isolate a 65% yield of benzoic acid from the ozonization products. This proves that hydrogen chloride adds to *cis*-phenylbutadiene in the 3,4-positions.

The hydrogen chloride could add to the 3,4-double bond of *cis*-phenylbutadiene to give either 1-phenyl-3-chloro-Δ^1-butene or 1-phenyl-4-chloro-Δ^1-butene. In addition to benzaldehyde,

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[1] Riiber, *Ber.*, **44**, 2974 (1911).

[2] Muskat and Herrman, THIS JOURNAL, **53**, 260 (1931).