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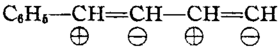
(1) Riiber, *Ber.*, **44**, 2974 (1911).

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

the former compound would yield on ozonization and subsequent hydrolysis, 1-chloropropionic aldehyde; while the latter compound would yield 2-chloropropionic aldehyde. A considerable quantity of the chloride was subjected to ozonization and the ozonized products worked up in the usual manner. It was possible to isolate and identify 1-chloropropionic aldehyde from the ozonization products. This proves that hydrogen chloride is absorbed in the 3,4-positions to give 1-phenyl-3-chloro-Δ^1-butene.

The *cis* - 1 - phenyl - 3 - chloro - Δ^1 - butene was washed with 10% sodium hydroxide: hydrogen chloride was eliminated and *cis*-phenylbutadiene was obtained. The *cis*-1-phenyl-3-chloro-Δ^1-butene was refluxed with a water suspension of silver oxide; *cis*-1-phenyl-3-hydroxy-Δ^1-butene was isolated and identified.

The addition of hydrogen chloride to the 3,4-positions of the geometric isomers of phenylbutadiene to give 1-phenyl-3-chloro-Δ^1-butene confirms the work of Riiber on the addition of hydrogen bromide to phenylbutadiene, and is in agreement with the theories of Muskat and his collaborators on the addition reactions of conjugated systems. According to Muskat and Becker[3] the electronic structure of phenylbutadiene is best represented as[4]



$$C_6H_5\text{—}\underset{\oplus}{CH}{=}\underset{\ominus}{CH}\text{—}\underset{\oplus}{CH}{=}\underset{\ominus}{CH_2}$$

Consequently the orientation of the hydrogen chloride in the 3,4-positions should give a 3-chloro rather than a 4-chloro derivative. This is confirmed by the experimental data reported in this paper.[5]

It is interesting to note that the difference in stability of the *cis* and *trans* chlorides is similar to the difference in stability already reported by Muskat and Herrman for the corresponding carbinols.[2]

Experimental Part

Trans-1-phenyl-3-chloro-Δ^1-butene.—Thirty grams of *trans*-phenylbutadiene, prepared according to the method of Muskat and Herrman,[6] was dissolved in anhydrous ether and dry hydrogen chloride gas was passed into the solution for several hours. The flask was immersed in a salt–ice bath during the reaction. The ethereal solution was washed with water until the last trace of acid was removed, dried over anhydrous sodium sulfate and distilled under reduced pressure. The slightly yellow oil distilled at 103° under 5 mm. pressure.

Anal. Calcd. for $C_{10}H_{11}Cl$: Cl, 21.29. Found: Cl, 21.34, 21.47.

Five grams of this hydrogen chloride addition product was dissolved in carbon tetrachloride and a current of ozonized oxygen was bubbled through the solution until oxidation was complete. After removal of the carbon tetrachloride under diminished pressure, the ozonide was decomposed with water. To assure complete decomposition the solution was warmed on the water-bath for two hours. The mixture consisting of acids and aldehydes was extracted several times with ether. The combined ether extracts were washed with dilute sodium carbonate solution to remove any acids present. The ethereal solution was dried and the ether removed by vaporization. The residual oil was treated with an aqueous solution of semicarbazide hydrochloride containing enough sodium acetate to render the solution neutral. A semicarbazone (2.2 g.) was precipitated after a short time. It was recrystallized several times from alcohol and melted at 214°, the melting point of the semicarbazone of benzaldehyde. A mixture with a sample of known origin also melted at 214°.

The combined alkaline extracts containing the acid fraction were acidified with sulfuric acid and extracted with ether. The ether solution was dried over sodium sulfate and the ether was removed by vaporization. A solid remained (1.05 g.) which, after recrystallization from alcohol, melted at 122°, the melting point of benzoic acid. A mixture with a sample of known benzoic acid also melted at 122°. The combined yield of benzoic acid and the semicarbazone of benzaldehyde was 72.8%.

Cis-1-phenyl-3-chloro-Δ^1-butene.—Thirty grams of *cis*-phenylbutadiene, prepared according to the method of Muskat and Herrman,[6] was treated with hydrogen chloride and worked up exactly as described above for the *trans* isomer. The product was distilled under reduced pressure; a small portion distilled over at 65–70° under 5 mm. pressure, while the remainder distilled at 106° under 5 mm. pressure. The low boiling distillate was phenylbutadiene. The higher boiling product was analyzed for chlorine and proved to be a monohydrogen chloride addition compound of phenylbutadiene.

Anal. Calcd. for $C_{10}H_{11}Cl$: Cl, 21.29. Found: Cl, 20.14, 19.97.

Upon repeated distillations the chloride decomposed completely into phenylbutadiene and hydrogen chloride. A number of attempts were made to prepare a pure chloride by using different solvents, such as glacial acetic acid, chloroform and carbon tetrachloride. In several experiments the chloride was prepared without the use of any solvent, but in no case were we able to prepare a chloride that was purer than the one described above.

The hydrogen chloride derivative (5 g.) was dissolved in chloroform and ozonized in the usual manner. After the removal of the chloroform, the ozonide was treated with

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(3) Muskat and Becker, THIS JOURNAL, **52**, 812 (1930).

(4) The plus and minus signs do not imply a complete transfer of an electron from one atom to another. They indicate merely a displacement of the electrons from their central positions. We are using the encircled plus and minus signs to differentiate them from ionic charges.

(5) We wish to emphasize that in representing the electronic polarity of these unsaturated compounds we are not referring to the *reactivity* of the double bonds but rather to the electronic orientation in the compound.

(6) Muskat and Herrman, THIS JOURNAL, **53**, 252 (1931).

30% hydrogen peroxide. The solution was allowed to stand at room temperature for one hour, after which it was heated on the water-bath for two hours. The solution was made alkaline with sodium carbonate and extracted with ether. The ether extract was dried and the ether removed. The residual oil distilled over at 86° under 11 mm. pressure; this was proved to be phenylbutadiene, and must have been formed from the decomposition of some of the chloride which was not ozonized. One and one-half grams of phenylbutadiene was recovered. The combined alkaline extracts were acidified with dilute sulfuric acid. Benzoic acid (1.5 g.) was precipitated. This was proved by its melting point and a melting point of a mixture with known benzoic acid. The yield of benzoic acid was 65%.

In another experiment a considerable quantity of the chloride was ozonized in chloroform solution. Alkali was not used in working up the ozonide, since it was shown that alkali readily removes hydrogen chloride from the compound. The ozonide was therefore decomposed by warming its aqueous solution on the water-bath, and then extracted with ether. The ether solution was dried, the ether removed by vaporization, and the residual oil was distilled. The largest portion distilled over between 79–86°. This was proved to be α-chloropropionic aldehyde by analysis and oxidation to acetic acid with alkaline permanganate. This differentiates it from the β-isomer which boils at 125–130° and easily polymerizes.

Cis-1-phenyl-3-chloro-Δ^1-butene was shaken for ten minutes with 10% sodium hydroxide at room temperature. The reaction mixture was extracted with ether, the ethereal solution dried, the solvent removed by vaporization and the residual oil distilled under reduced pressure. The major portion of the oil distilled over at 86° under 11 mm. pressure, which is the boiling point of *cis*-phenylbutadiene.

Cis-1-phenyl-3-chloro-Δ^1-butene was refluxed with an excess of silver oxide suspended in water until no further reaction occurred. The reaction mixture was extracted with ether, the ethereal solution dried, the solvent removed by vaporization and the residual oil distilled under reduced pressure. The oil distilled at 144° under 21 mm. pressure, which is the boiling point of *cis*-1-phenyl-3-hydroxy-Δ^1-butene. The identity of this carbinol was further proved by its reactions.[6]

Summary

The mono-hydrogen chloride addition products of the two geometric isomers of 1-phenylbutadiene were prepared and their structures proved. In each case addition occurred in the 3,4-double bond to give 3-chloro derivatives. This is in complete accord with the electronic theories of Muskat and his collaborators on the addition reactions of conjugated systems.

NEW YORK, N. Y. RECEIVED FEBRUARY 20, 1934

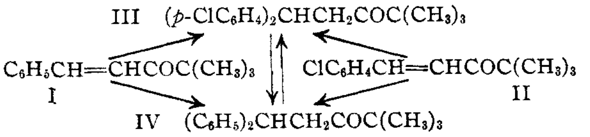
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reversibility of the Friedel–Crafts Reaction. The Interconversion of α-(Benzohydryl)-pinacolones

BY HARRY H. WEINSTOCK, JR., AND REYNOLD C. FUSON

The theory that the addition of aromatic compounds to α,β-unsaturated carbonyl compounds in the presence of aluminum chloride and hydrogen chloride[1] is reversible leads to the prediction that β,β-diaryl carbonyl compounds of the type $(Ar)_2CHCH_2CO—$ should be interconvertible according to the equation $(Ar)_2CHCH_2CO— + 2Ar'H = (Ar')_2CHCH_2CO— + 2ArH$. An interconversion of this type has now been realized.

For this work the α-(benzohydryl)-pinacolones have been selected; this was partly because of their ready accessibility and partly on account of the fact that the tertiary butyl group, unlike aryl groups, cannot lead to the formation of indanones.



Preliminary exploration in this field showed that the benzalpinacolones behaved in a manner very similar to that previously outlined for the benzalacetophenones.[1b] Benzalpinacolone (I), and *o*- and *p*-chlorobenzalpinacolones (II) were found to yield α-(benzohydryl)-pinacolone (IV) when treated with benzene, and α-(*p*,*p*′-dichlorobenzohydryl)-pinacolone (III) when chlorobenzene was used. The conversion of benzalpinacolone to III was remarkable because it was the first instance in which a phenyl group had been replaced. Moreover, it foreshadowed the interconversion of III and IV—a result which depended on such a replacement.

The conversion of III into IV, as already intimated, was accomplished by treatment of the dichloro compound with benzene, aluminum chloride and hydrogen chloride. This process could be *reversed* by subjecting IV to the action of chlorobenzene, aluminum chloride and hydrogen

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[1] (a) Fuson, Kozacik and Eaton, THIS JOURNAL, **55**, 3799 (1933); (b) Eaton, Black and Fuson, *ibid.*, **56**, 687 (1934).