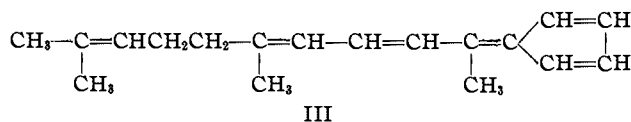
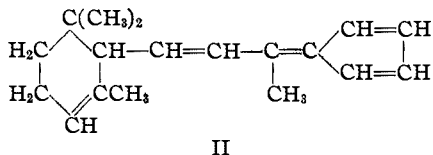
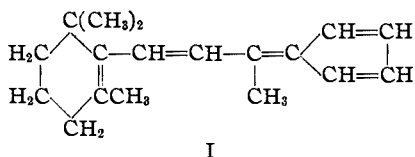


[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Fulvenes in the Ionone Series

BY E. P. KOHLER AND JOHN KABLE

In view of a recent publication in which Willstaedt¹ announced the preparation of a fulvene from β -ionone, it seems advisable to publish our own results in this field. In 1932 we began a study of the condensation of cyclopentadiene with beta, alpha and pseudo ionone with a view to the preparation of substances similar in type to carotin and to vitamin A. By the time the work was temporarily interrupted in 1933 we had prepared and to some extent studied the three fulvenes represented by the following formulas.



These formulas are based upon the method of preparation, analyses and the quantity of hydrogen absorbed in catalytic hydrogenation. The fulvene obtained from β -ionone (I) was also ozonized; as was to be expected, geronic acid was one of the products.

All three hydrocarbons are viscous, highly colored oils which can be distilled under low pressures but resinify rapidly at temperatures but little above 100°. They undergo autoxidation more rapidly than any known fulvenes, the product from pseudo ionone (III) being especially sensitive to atmospheric oxygen. Like the simpler fulvenes they form solid peroxides on prolonged exposure to oxygen.

In the hope of converting these oils into solids that would be more suitable for identification we treated them with maleic anhydride. The behavior of all three substances was peculiar in that the color, instead of becoming lighter or disappear-

ing as it does with simpler fulvenes, steadily became deeper during the reaction with the anhydride. No crystalline products were obtained and the course of the reaction has not yet been established.

The behavior of these hydrocarbons on catalytic hydrogenation is similar to that of the carotinoids. They rapidly combine with two atoms of hydrogen and become colorless. Further hydrogenation is much slower and for complete hydrogenation it is necessary to employ the same relatively large quantities of catalyst that are required for the complete hydrogenation of carotinoids. The intermediate dihydro compounds are easily dehydrogenated under the same conditions under which Kuhn and Drumm² observed the dehydrogenation of bixin and crocetin. The hydrocarbons also give the same or very nearly the same color reactions as carotin and vitamin A.

Experimental Part

Fulvene from β -Ionone, I.—A mixture of 57.7 g. of pure β -ionone and 19.8 g. of freshly distilled cyclopentadiene was added slowly, with constant shaking and when necessary with cooling, to a solution of 6.9 g. of sodium in 85 cc. of absolute methyl alcohol. As soon as all of the material had been added, the resulting mixture was poured into water and the condensation product was extracted with chloroform. The chloroform solution was dried with sodium sulfate and fractionated under diminished pressure. The product boiled at 111–113° (0.5 mm.) and the yield was 57.5 g. or 80%.

Anal. Calcd. for $\text{C}_{18}\text{H}_{24}$: C, 89.9; H, 10.1. Found: C, 89.6; H, 10.1.

The fulvene is a viscous, orange-colored oil. It rapidly absorbs oxygen from the air and is converted into a resin. When a chloroform solution of antimony trichloride—prepared like the solutions used for detecting vitamin A—is added to a dilute solution of the fulvene in the same solvent (less than 0.01 mg. in 3 cc.) it produces a blue color that is scarcely distinguishable from that developed by vitamin A.

Ozonization.—A current of ozonized oxygen was passed through an ice-cold solution of 1.9 g. of the fulvene in 40 cc. of carbon tetrachloride for twenty-four hours. The resulting amorphous ozonide was removed, dissolved in glacial acetic acid and treated with ozonized oxygen for another six hours. The resulting solution, manipulated according to the method of Karrer and Morf,³ gave 0.12 g. of the semicarbazone of geronic acid—identified by comparison with an authentic specimen.

(2) Kuhn and Drumm, *Ber.*, **65**, 1458 (1932).

(3) Karrer and Morf, *Helv. Chim. Acta*, **14**, 1033 (1931).

(1) Willstaedt, *Chem. Abs.*, **28**, 3720 (1934).

Hydrogenation.—A suspension of 0.26 g. of platinum oxide in 15 cc. of ethyl acetate was shaken with hydrogen until the reduction was complete. After adding 0.14 g. of the fulvene the shaking was continued until no more hydrogen was absorbed. The solution became colorless long before hydrogenation was complete. The substance combined with 62 cc. of hydrogen instead of 65 cc. calculated for 5 double linkages and the product no longer reduced a solution of permanganate in acetone. In a similar experiment it was found that the solution became colorless when two atoms of hydrogen had been absorbed. The operation was interrupted at this stage and the product was isolated in the usual manner. A solution of the resulting colorless oil in piperidine rapidly developed color when it was shaken with air and the residue that was left after removing the solvent gave the characteristic color reactions of the fulvene.

Reaction with Maleic Anhydride.—A solution of 4.8 g. of the fulvene in 10 cc. of pure benzene was treated with 2.0 g. of maleic anhydride. A reaction accompanied by slight evolution of heat occurred at once. The color of the solution, originally orange, darkened rapidly and became a very dark red when the mixture was warmed for a few minutes on a steam-bath. Quinone, which like maleic anhydride forms beautifully crystalline addition products with cyclopentadiene, caused the same color changes as the anhydride, but no crystalline addition products could be obtained with either of these substances.

Fulvene from α -Ionone, II.—Condensation of pure α -ionone with cyclopentadiene by the same procedure that was used with the β -isomer resulted in a product which boiled at 107–109° under 5 mm. The yield was 76%.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.9; H, 10.1. Found: C, 89.5; H, 10.2.

This fulvene is likewise a viscous, orange-colored oil which rapidly absorbs oxygen from the air. Like the β -isomer it becomes colorless after absorbing two atoms of hydrogen and requires 10 atoms of hydrogen for complete saturation. Like its isomer, also, it is regenerated when a piperidine solution of the dihydro addition product is shaken with air. The color produced by antimony chloride is a shade of blue slightly different from that obtained with the β -isomer.

Fulvene from Pseudo-ionone, III.—This fulvene was obtained like the others but owing to resinification during distillation the yield of pure product was much lower—38%. It boiled at 139–141° under 0.5 mm.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.9; H, 10.1. Found: C, 89.6; H, 10.2.

The fulvene is a viscous, red oil. It becomes colorless after combining with two atoms of hydrogen and requires 12 atoms for complete saturation. Its behavior toward maleic anhydride is the same as that of the other fulvenes of this series and like the others it develops a blue color with antimony chloride.

Summary

The paper contains a description of the method that was found best for condensing the ionones with cyclopentadiene and a brief description of the resulting fulvenes.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

The Structure of Rubber and the Mechanism of Elastic Stretching

BY EDWARD MACK, JR.

Rubber seems to be unique in the magnitude of its elastic extensibility. No adequate explanation of its behavior has ever been given.

The supposition that mere high molecular weight alone can account for pronounced elastic properties is not permissible. High molecular weight may be *necessary* but it is not a *sufficient* condition. In any elastic-stretch effect, at all comparable in magnitude with that of rubber, we must necessarily expect to find *two* features present, whatever the particular mechanisms may be by means of which these two features are achieved, namely: (I) there must be some mechanism whereby the molecules involved can change their width and depth dimensions into length, upon the application of a stretching force; and (II) there must be some mechanism for automatic retraction.

The closest approach to a satisfactory picture is perhaps Kirchhof's assumption of a spiral¹ molecule, later developed by Fikentscher and Mark,² Hauser³ and others. Although this explanation may have provided satisfactorily for (I), it has been weak and defective in the more essential particular, since it has failed to indicate any operable mechanism for automatic retraction.

In the first place, when we examine into the potentialities of the rubber molecule in a search for centers of attractive force sufficiently cogent to implement a mechanism for compulsory folding, we are practically limited to a consideration of two possibilities: either (a) that the residual

(1) Kirchhof, *Kolloid Z.*, **30**, 176 (1922); *Kolloidchem. Beihefte*, **16**, 47 (1922).

(2) Fikentscher and Mark, *Kautschuk*, **6**, 2 (1930); *Rub. Chem. and Tech.*, **3**, 201 (1930).

(3) Hauser, 76th Meeting of the American Chemical Society, and *Ind. Eng. Chem.*, **21**, 249 (1929).