paleographic map can be made from any of the published maps in fifteen to twenty minutes. Since this method is both rapid and inexpensive, it is possible to have a large number of these maps illustrating not only periods but all important epochs of a period. The writer has found that not only do students grasp many of the facts of historical geology better by this method but that its use greatly adds to the pleasure of both the student and instructor.

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SPECIAL ARTICLES

THE STRUCTURE OF VITAMIN A AND THE SYNTHESIS OF IONENES

THE brilliant investigations of the past two or three years, here as well as abroad, on the chemical nature of vitamin A, which culminated in the structural formula (I) proposed a year ago by Karrer, Morf and Schöpp,[1] have directed increasing attention to this compound and its remarkable properties.

An article, dealing with the constitution of vitamin A, by Heilbron, Morton and Webster,[2] which has just appeared, leads us to report immediately and briefly the results of our own recent studies of this problem.

Heilbron, Morton and Webster distilled vitamin A concentrate with finely powdered selenium and obtained 1,6-dimethylnaphthalene (VI) as one of the principal products. As a possible explanation of this reaction, they suggest the preliminary cyclization of the vitamin to a hydronaphthalene derivative (II), which then breaks down to ionene (III), for Ruzicka and Rudolph[3] have shown that when ionene is distilled with sulfur 1,6-dimethylnaphthalene results and, as is well known, the action of sulfur in such distillations is similar to that of selenium.

It is obvious that, whatever the mechanism may be by which ionene is formed from the vitamin, the value of this observation of Heilbron, Morton and Webster's, in throwing light upon the constitution of the vitamin, depends upon the establishment of the constitution of ionene itself, and that is one of the phases of this vitamin problem which our organic laboratories at Columbia University have been studying for some time and which we believe that we have now brought to a successful conclusion, through the investigations of Dr. David Davidson and Messrs. Victor G. Fourman and Percy M. Apfelbaum.

Ionene was discovered by Tiemann and Krüger[4] by the dehydration of *alpha*-ionone, or of a mixture of *alpha*- and *beta*-ionones. Later, Tiemann[5] showed that it could be prepared also from *beta*-ionone.

On the basis of the products obtained from it by oxidation, Tiemann and Krüger were disposed first to assign to ionene constitution (IV), but finally decided in favor of formula (V).

Three years later, Barbier and Bouveault,[6] proposed the structure (III) as the more probable one for ionene, but cited no new experimental work in support of this opinion. Tiemann,[7] in reply to Barbier and Bouveault, insisted upon the correctness of his own formula (V) and quoted his original oxidation experiments.

Baeyer and Villiger[8] investigated the constitution of ionene, by their exhaustive bromination method, confirmed the existence of the carbon skeleton common to all three of the suggested ionene formulas, but threw no light upon the location of the double bonds.

Auwers and Eisenlohr,[9] as the result of their study of the molecular refractivity of ionene, decided in favor of (IV) rather than (V), but apparently failed to consider (III) at all.

In the course of their researches in the naphthalene field, Ruzicka and Rudolph[3] distilled ionene with sulfur, as noted above, and obtained 1,6-dimethylnaphthalene, using the Barbier and Bouveault formula (III) to illustrate the reaction. A year later, in his brochure[10] on the sesquiterpenes, Ruzicka accepted the carbon skeleton of the ionene formula as proven, but the location of the double bonds as still unknown.

It is our belief that we have now cleared up this uncertainty, and established the complete constitution of ionene, by the results of the following investigations:

I. Mr. Fourman, by a careful study of the nitro, nitroamino and sulfo derivatives, the oxidation products of ionene itself and of its dinitro derivatives, has made it quite evident that the Barbier and Bouveault formula (III) for ionene is correct.

II. Davidson and Apfelbaum have now demonstrated the accuracy of this deduction by the synthesis of ionene through these steps:

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[1] Karrer, Morf and Schöpp, *Helv. Chim. Acta.*, 14, 1434 (Dec., 1931).

[2] Heilbron, Morton and Webster, *Biochem. J.*, 26, 1194.

[3] Ruzicka and Rudolph, *Helv. Chim. Acta.*, 10, 918 (1927).

[4] Tiemann and Krüger, *Ber.*, 26, 2693 (1893).

[5] Tiemann, *Ber.*, 31, 873 (1898).

[6] Barbier and Bouveault, *Bull. soc. chim.* [3], 15, 1008 (1896).

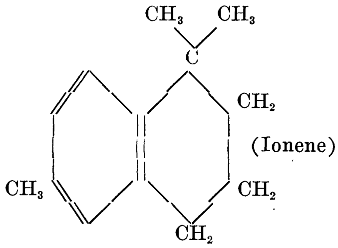
[7] Tiemann, *Ber.*, 31, 854 (1898).

[8] Baeyer and Villiger, *Ber.*, 32, 2429 (1899).

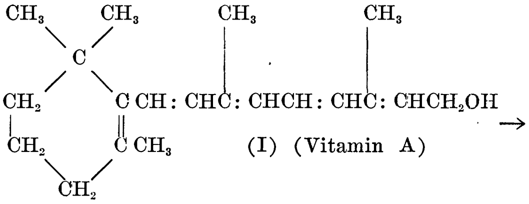
[9] Auwers and Eisenlohr, *J. prakt. Chem.* [2], 84, 61 (1911).

[10] "Über Konstitution und Zusammenhänge in der Sesquiterpenreihe," *Fortschr. d. Chem., Phys. u. phys. Chem.*, 19, No. 5, p. 9 (1928).

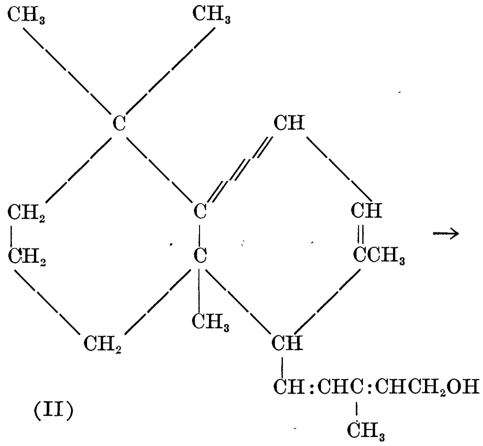
$(m)CH_3C_6H_4CHO$
$\downarrow + CH_3COOR$
$CH_3C_6H_4CH:CHCOOR$
$\downarrow + Na + C_5H_{11}OH$
$CH_3C_6H_4CH_2CH_2CH_2OH$
$\downarrow + HBr$
$CH_3C_6H_4CH_2CH_2CH_2Br$
$\downarrow$ + Grignard
$CH_3C_6H_4CH_2CH_2CH_2C(CH_3)_2OH$
$\downarrow + H_2SO_4$



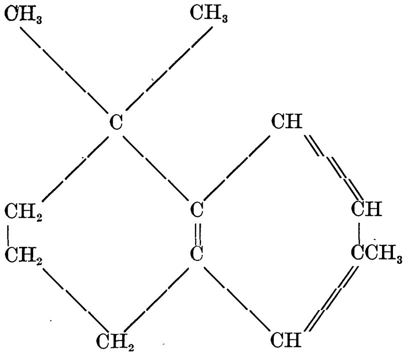
(Ionene)



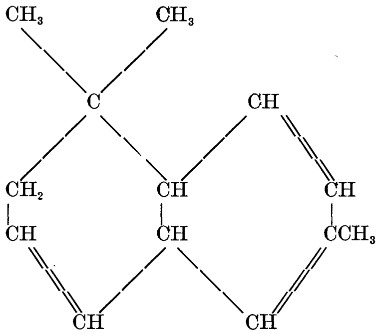
(I) (Vitamin A)



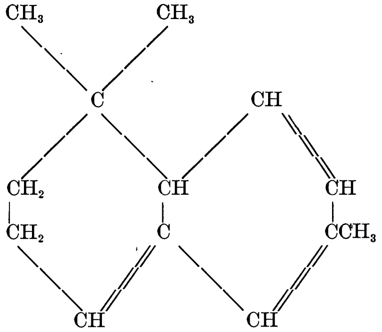
(II)



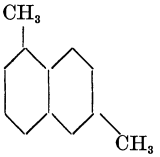
(III) (Ionene)



(IV)



(V)



(VI) (1, 6-Dimethylnaphthalene)

The ionene so synthesized is identical in all respects with that prepared by the dehydration of either *alpha*- or *beta*-ionone, and we have already utilized similar reactions for the synthesis of other ionenes and analogously constituted compounds.

Detailed articles describing these syntheses in full, as well as the work of Mr. Fourman, will be published elsewhere and will appear shortly.

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