

NATURAL DERIVATIVES OF FURAN

II. THE STRUCTURE OF EVODONE

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Summary

2-Acetyl-5-methylcyclohexan-1,3-dione (IV) has been synthesized and is probably identical with a degradation product of evodone. On the basis of this synthesis and of published work, evodone is probably III.

I. INTRODUCTION

Evodone, $C_{10}H_{12}O_2$, $[\alpha]_D^{26} -53.9^\circ$, m.p. $73^\circ C$, was isolated from *Evodia hortensis* Forst. by van Hulssen (1941). The substance is an unsaturated ketone, λ_{max} . 265 $m\mu$, $\log \epsilon_{max}$. 3.57, and on oxidation with permanganate gives methylsuccinic acid. Ozonolysis produces a compound, $C_9H_{12}O_3$ (according to published analyses; $C_9H_{10}O_3$ is erroneously given in several places), m.p. $42.5^\circ C$, which gives a ferric colour and has λ_{max} . 270 $m\mu$, $\log \epsilon_{max}$. 3.94. Hydrogenation gives a mixture including a substance $C_{10}H_{16}O_2$, m.p. $160^\circ C$ which is still a ketone, and reduction under Clemmensen conditions and oxidation gives β -methyladipic acid. Among the products of ozonolysis is stated to be formaldehyde, but no indications of amount or method of detection are given. van Hulssen considered evodone to have formula I.

A more satisfactory formula appears to us to be III. Against I are several indications. The ozonolysis product II should have the formula $C_9H_{10}O_3$, instead of $C_9H_{12}O_3$ which analyses clearly indicate; there also seems no reason why II should give a ferric test. The ultraviolet absorption maximum of II would probably not be at longer wavelengths than 245 $m\mu$; the figure found is 270 $m\mu$. The 2,4-dinitrophenylhydrazone of evodone has m.p. $258-260^\circ C$, which is in the range found for aromatic ketones; from general experience the derivative of I would be expected to have a m.p. at least a hundred degrees lower than this.

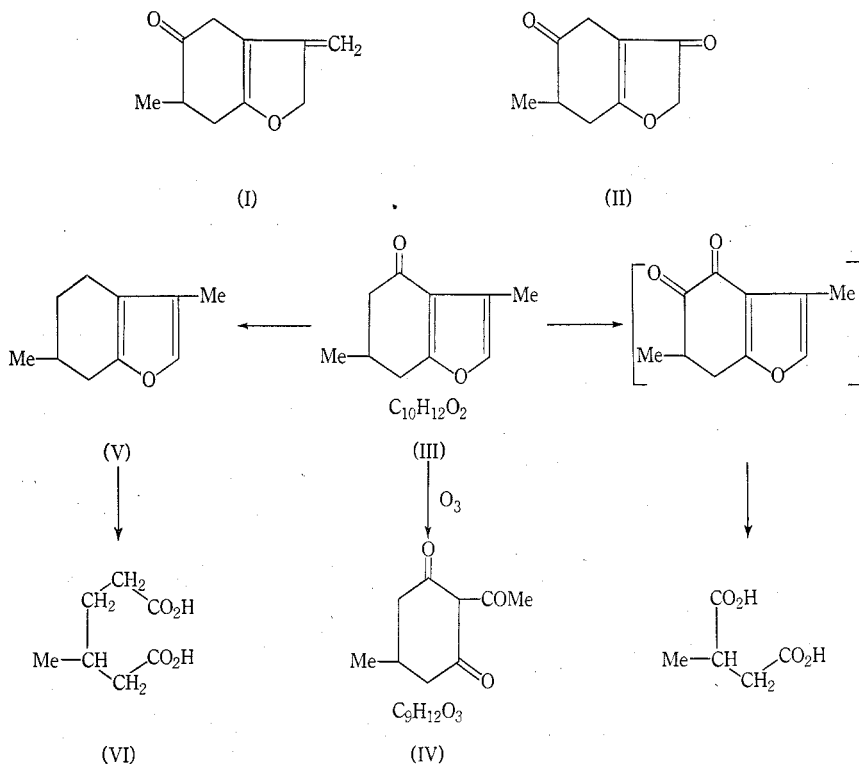
Structure III explains all the known reactions and properties of evodone, except the formation of formaldehyde on ozonolysis. In the absence of evidence as to the amount formed, this observation must be treated with reserve, since small amounts of formaldehyde frequently result from the ozonolysis of compounds not containing $C=CH_2$. The nearest analogue of III, of which the ultraviolet spectrum is recorded in the literature, is 2-acetylfuran, which has λ_{max} . 266-267 $m\mu$ (Abe 1938) (cf. evodone λ_{max} . 265 $m\mu$). 2-Acetyl-5,5-dimethylcyclohexan-1,3-dione has an absorption band at 277 $m\mu$, $\log \epsilon$ 4.0 (Birch and

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Todd 1952); the ozonolysis product now formulated as IV has $\lambda_{\text{max.}}$ 270 m μ , $\log \epsilon_{\text{max.}}$ 3.94. The product of Clemmensen reduction of III would be menthofuran (V) which is known to give β -methyladipic acid (VI) on oxidation (Wienhaus and Dewein 1934).

Clearly IV is the key-compound and its synthesis was undertaken by standard methods. Orcinol dimethyl ether was reduced with sodium and ethanol in liquid ammonia to the 2,5-dihydro-derivative (cf. Birch 1950), and acid hydrolysis gave 5-methylcyclohexan-1,3-dione. This was refluxed with acetic anhydride-sodium acetate to form 2-acetyl-5-methylcyclohexan-1,3-dione (IV), m.p. 42.5–44 °C with absorption maxima at 235 m μ , log ϵ 3.83 and 270 m μ ,



log ϵ 4.11, giving the expected red ferric test. These properties agree with those found by van Hulssen for the ozonolysis product of evodone. He did not examine the ultraviolet spectrum in the region of 235 m μ . We have so far been unable to obtain authentic evodone, but we are convinced on the above evidence that the formula is in fact III, and attempts to synthesize this substance are in progress. Evodone is therefore probably a ketomenthofuran, and another member of the series of natural furans related to terpenes.

II. EXPERIMENTAL

Orcinol dimethyl ether (7.4 g) in ethanol (20 c.c.) and liquid ammonia (100 c.c.) was reduced by adding sodium (5 g) in small pieces over 10 min with swirling. Water (75 c.c.) was added, the product taken up in ether, dried over potassium carbonate, the ether evaporated, and the

residue heated on the steam-bath for 10 min with N hydrochloric acid (5 c.c.). The product was taken up in ether (35 c.c.) and extracted with sodium hydroxide solution (5%). Acidification and extraction with ether gave 5-methylcyclohexan-1,3-dione (4.4 g) which crystallized on evaporation of the ether and was recrystallized from water, m.p. 127–128 °C (Found: C, 66.7; H, 8.0%. Calc. for $C_7H_{10}O_2$: C, 66.6; H, 8.0%). This substance (2.0 g), acetic anhydride, and anhydrous sodium acetate (3.0 g) were refluxed for 3 hr, the excess of anhydride decomposed with water, and the solution extracted with ether. After washing the extract with saturated bicarbonate solution, the product was extracted with aqueous sodium hydroxide (5%). Acidification and ether extraction gave an oil which solidified in ice, and was recrystallized twice from light petroleum (b.p. 60–90 °C) (ice-cooling) and then from aqueous ethanol. The 2-acetyl-5-methylcyclohexan-1,3-dione (0.90 g) formed colourless glistening plates, m.p. 42.5–44 °C (Found: C, 64.2; H, 7.2%. Calc. for $C_9H_{12}O_3$: C, 64.3; H, 7.2%).

III. REFERENCES

- ABE, S. (1938).—*J. Chem. Soc. Japan* **59**: 1117.
BIRCH, A. J. (1950).—*Quart. Rev. Chem. Soc. Lond.* **4**: 69.
BIRCH, A. J., and TODD, A. R. (1952).—*J. Chem. Soc.* **1952**: 3102.
VAN HULSEN, C. J. (1941).—*De Ing. Nederland-Indie* **8**: 89. (cf. *Chem. Abstr.* **36**: 4970.)
WIENHAUS, H., and DEWEIN, H. (1934).—*Z. Angew. Chem.* **47**: 415.