

CVI.—*The Action of Sulphuric Acid on Fenchone.*

By JAMES E. MARSH.

If fenchone is warmed with strong sulphuric acid, sulphur dioxide is given off and acetoxylenes [$\text{Me}:\text{Me}:\text{Ac}=1:2:4$] is formed. This compound has been obtained synthetically by Claus by the action of acetyl chloride on orthoxylenes in presence of aluminium chloride (*J. pr. Chem.*, 1890, [ii], 41, 396). Armstrong and Kipping (*Trans.*, 1893, 63, 75) obtained the same compound by the action of sulphuric acid on camphor; they found that camphor is not readily acted on by sulphuric acid at a temperature below 100° , that it was most advantageous to heat the mixture to 110° , that acetoxylenes is not the only product of the reaction, and that it was not practicable to separate the compound in a pure state by fractional distillation; they effected its separation by preparing the crystalline phenylhydrazones from it and decomposing this by hydrolysis.

When fenchone was warmed with five times its volume of strong sulphuric acid, the action began at a temperature below 50° with evolution of sulphur dioxide. The evolution of gas was rapid at 80° , and at 100° was complete in a few minutes. I used small quantities of not more than 10 c.c. of fenchone in one operation. It appeared preferable to keep the temperature at about 80° , and there was little or no charring. After cooling, the solution was poured into water and distilled in steam. The distillate was shaken out with ether and the ethereal solution distilled under reduced pressure. After the ether and water had come off without condensing, the residue distilled almost entirely at 131° under 20 mm. pressure; it amounted to about 70 per cent. of the fenchone taken. If we take into consideration the loss arising from the number of operations which the fenchone had undergone, and that only 10 grams were used, the yield of acetoxylenes probably approximates to that required by theory. It was redistilled and the fraction boiling at 131° under 20 mm. pressure was analysed. It gave

$\text{C}=80.6$; $\text{H}=8.3$. $\text{C}_{10}\text{H}_{12}\text{O}$ requires $\text{C}=81.0$; $\text{H}=8.1$ per cent.

The acetoxylenes so obtained was a nearly colourless oil smelling somewhat of cinnamon. Its specific gravity was found to be 0.9968 at $20^\circ/4^\circ$. When treated with hydroxylamine hydrochloride and caustic potash in alcoholic solution, it gave a good yield of the oxime which crystallised from methylic alcohol, forming colourless crystals melting at $86-87^\circ$. Claus gives the melting point at $88-89^\circ$, Armstrong and Kipping at $84.5-85.5^\circ$.

To further establish its identity and constitution, a small quantity

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was oxidised by warming gently with a slight excess of bromine dissolved in 4 per cent. caustic soda solution, until bromine was scarcely liberated by addition of acid. On filtering from the crystals of carbon tetrabromide, and on addition of dilute sulphuric acid, a thick precipitate was thrown down which, after crystallising from dilute alcohol, melted at 163° . On analysis the product gave

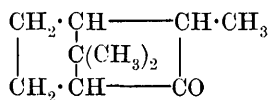
C = 71.6; H = 6.7. $C_9H_{10}O_2$ requires C = 72.0; H = 6.6 per cent.

The silver salt was prepared and, on analysis, gave

Ag = 41.8. $C_9H_9Me_2 \cdot COOAg$ requires Ag = 42.0 per cent.

The acid thus obtained by oxidation of acetoxylene is paraxylic acid [$CH_3:CH_3:COOH = 1:2:4$].

It seems reasonable to suppose that the almost quantitative conversion of fenchone into acetoxylene ought to have an important bearing on the constitution of fenchone. I have attempted in a paper on "The Constitution of Camphor" (*Trans. Oxford Univ. Jun. Sci. Club N.S.*, 1898, 110) to show how the formation of acetoxylene from camphor, established by Armstrong and Kipping, may be explained; I here only wish to point out that fenchone is probably still more nearly related in constitution to acetoxylene than is camphor, judging from the ease with which this compound is obtained from fenchone compared with the difficulty of its production from camphor. The following formula for fenchone was put forward last year by Wallach (*Annalen*, 1898, 300, 320) and by Gardner and Cockburn (*Trans.*, 1898, 73, 708) independently:



The coincidence of two separate lines of research leading to the same conclusion might be regarded as affording at least a presumption in favour of the formula. But the coincidence is less remarkable seeing that the formula is constructed on the model of Bredt's camphor formula. Further, neither Wallach nor Gardner and Cockburn express themselves as satisfied with the formula, and bring forward objections to it which seem to me not less convincing than their arguments in its favour. To these objections I think ought to be added the formation from fenchone of acetoxylene which it seems impossible to reconcile with the formula proposed.

I have from time to time ventured to criticise some of the formulæ proposed for members of the terpene group, partly on the ground that they do not account for the derivatives of benzene which are obtained from them by comparatively simple reactions. Nor does it seem to

me obvious why it should be regarded a sounder principle to base the constitution of closed chain compounds, such as the terpenes, on the products obtained by breaking down their cyclic structure, than on those products in which a ring remains. At present there seems to be an inclination either to disregard the latter entirely, or in certain cases to make a selection of those benzene derivatives which may be accounted for. It is not unreasonable to require that any constitution assigned to a member of the terpene group must account for both the aromatic and the fatty derivatives obtained from it.

I wish to thank Mr. Gardner and Mr. Cockburn for kindly giving me the samples of fenchone with which these experiments were made.

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