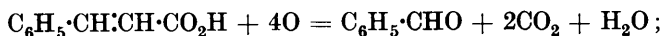


## NOTES.

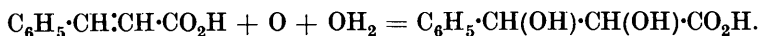
*Oxidation by Permanganate of an Unsaturated Substance, Cinnamic Acid.* By ERIC MAURICE STODDART.

CINNAMIC acid, in boiling 1% aqueous solution neutralised with caustic soda, was oxidised by the gradual addition of 2% aqueous potassium permanganate, of which the amount added was equivalent

to 3.50 per molecule of the acid. The benzaldehyde that volatilised corresponded (in the form of its phenylhydrazone) to oxidation of about 70% of the acid according to the equation :

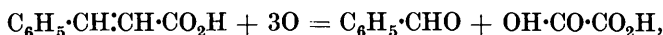


about 20% of the acid was recovered unchanged; and phenylglyceric acid was obtained in amount (crude) corresponding to oxidation of about 10% of the cinnamic acid according to the equation :



The formation of phenylglyceric acid in so considerable amount is interesting in view of the general impression that cooling with ice is necessary in order to effect oxidation by permanganate of an unsaturated substance without splitting its chain of carbon atoms at the double bond.

Among the products of oxidation carbonate was detected in abundance, but no oxalate. The absence of oxalic acid is remarkable in view of statements to the contrary in the literature, for the 3.50 employed, though in excess of the 3.0 required to effect oxidation to oxalic acid,



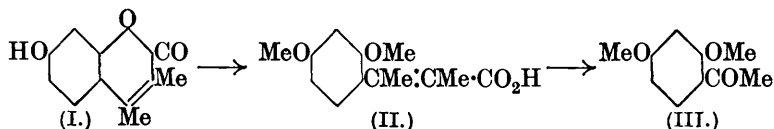
was in deficit of the 4.0 required to effect complete oxidation to carbon dioxide.—TECHNICAL COLLEGE, SUNDERLAND. [*Received, May 12th, 1931.*]

*The Conversion of 7-Hydroxy-3:4-dimethylcoumarin into 2:4-Dimethoxy- $\alpha\beta$ -dimethylcinnamic Acid.* By FREDERICK W. CANTER and ALEXANDER ROBERTSON.

SIMONIS and REMMERT (*Ber.*, 1914, **47**, 2229) assumed that the product of the condensation of resorcinol and methyl\*  $\alpha$ -methylacetoacetate in the presence of phosphoric oxide was 7-hydroxy-2:3-dimethyl-1:4-benzopyrone. In collaboration with Curd (this vol., p. 1255) we have shown that the compound obtained is 7-hydroxy-3:4-dimethylcoumarin (I) (Pechmann and Duisberg, *Ber.*, 1883, **16**, 2119). Conclusive proof that this compound is a

\* Owing to an error in transcription, Robertson and Curd (this vol., p. 1257) stated that Simonis and Remmert had used *ethyl*  $\alpha$ -methylacetoacetate in this condensation. Actually, they used the *methyl* ester, and the former authors found that both esters gave the same result.

coumarin is now afforded by its conversion into 2 : 4-dimethoxy- $\alpha\beta$ -dimethylcinnamic acid (II).



The methyl ether of (I) (6 g.) was prepared by means of methyl sulphate and sodium hydroxide and dissolved in a boiling mixture of methyl alcohol (50 c.c.) and 20% aqueous sodium hydroxide (50 c.c.). After cooling to 50°, the solution was agitated, and methyl sulphate (30 g.) gradually introduced. 20% Aqueous sodium hydroxide (100 c.c.) and a further quantity of methyl sulphate were then added. The reaction mixture was made faintly alkaline and the product was isolated by means of ether and hydrolysed by boiling with 75% alcohol (100 c.c.) containing potassium hydroxide (10 g.) for 2 hours. On cooling, the solution was diluted with water (200 c.c.) and acidified with concentrated hydrochloric acid. Next day the solid was collected and dissolved in aqueous sodium bicarbonate, and the solution filtered from unchanged 7-methoxy-3 : 4-dimethylcoumarin (1.8 g.). Acidification with hydrochloric acid gave the cinnamic acid (II) (4 g.), which crystallised from water in colourless rectangular plates or from benzene-ligroin in squat prisms, m. p. 133° [Found : C, 66.0; H, 6.9; OMe, 25.0; CO<sub>2</sub>H (by titration), 19.3. C<sub>11</sub>H<sub>10</sub>O<sub>2</sub>(OMe)<sub>2</sub> requires C, 66.1; H, 6.8; OMe, 26.3; CO<sub>2</sub>H, 19.1%]. The substance is easily soluble in alcohol or benzene and sparingly soluble in water. It decolorises bromine water and aqueous potassium permanganate.

The acid (2 g.) was dissolved in warm acetone (80 c.c. at 50°) and oxidised by the addition of 1.4% solution of aqueous potassium permanganate (200 c.c.). The cooled mixture was cleared with sulphur dioxide, and the product isolated by means of ether. Removal of the solvent left 2 : 4-dimethoxyacetophenone (III) as an oil which partly solidified. The semicarbazone crystallised from methyl alcohol in tiny plates, m. p. 202—203° after slight sintering at 198°, and was identical with the semicarbazone prepared from an authentic specimen of the ketone.—LONDON SCHOOL OF HYGIENE AND TROPICAL MEDICINE, UNIVERSITY OF LONDON. [Received, May 21st, 1931.]