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Received December 22, 1958.

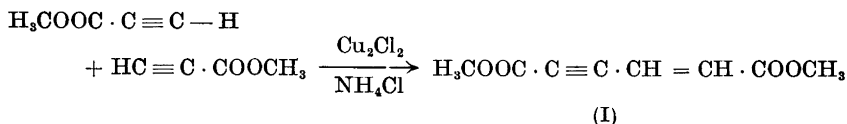
Cuprous Chloride Catalysed Dimerisation of Methyl Propiolate

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In an attempt to prepare methyl deca-2:4-diyne by the so-called Glaser coupling¹ of methyl propiolate with *n*-hept-1-yne, Christensen and Sørensen² were able to obtain only tetradeca-6:8-diyne and two crystalline substances which analysed for C₈H₈O₅ and C₈H₈O₆, respectively. In order to determine the structures of these two anomalous products the Glaser coupling of methyl propiolate was investigated.

The reaction of methyl propiolate in slightly acidic aqueous cuprous chloride-ammonium chloride solution, with air as the oxygen source, gave a crystalline compound in 36 % yield. The substance



was obtained as colourless thick needles from ether-petroleum ether, m.p. 57°. (Found: C 57.40; H 5.04. Calc. for C₈H₈O₄; C 57.14; H 4.80). U.V.-absorption, in ethanol: λ_{max} 2 660, 2 540, 2 440 (inflection) Å. ε 12 900, 17 500, 16 300. The infrared spectra showed the presence of acetylenic and ethylenic bonds in addition to bands characteristic of an ester. A strong band

at 958 cm⁻¹ indicated that the double bond had the *trans* configuration.³ On the basis of this evidence we concluded that the substance was dimethyl hex-2-en-4-yne-1:6-dioate (I). This compound has been reported in the literature.⁴ There are, however, small discrepancies in the melting points and ultraviolet spectra of the two compounds, but these may be due to a difference in the configuration about the double bond.

The formation of the compound can be explained by addition of one molecule of methyl propiolate to another, thus being an example of a substituted acetylene undergoing the Nieuwland dimerisation.⁵ Accordingly oxygen should not play any part in the reaction. This was confirmed by running the reaction under pure nitrogen, when practically the same yield of (I) was obtained.

Just after the completion of this work, Akhtar and Weedon⁶ published a report on the reaction of substituted copper acetylides with oxygen in hot acetic acid. They obtained the corresponding vinyl acetylenic compounds in good yields.

Further work on this reaction is in progress.

Acknowledgement. I am indebted to Professor N. A. Sørensen for his interest in this work.

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Received December 18, 1958.

Acta Chem. Scand. **13** (1959) No. 1