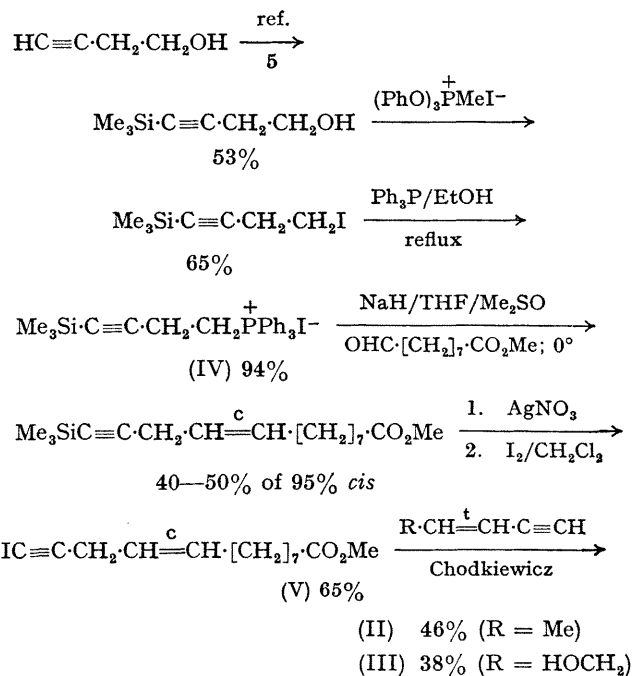
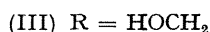
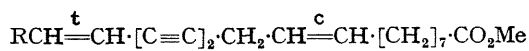
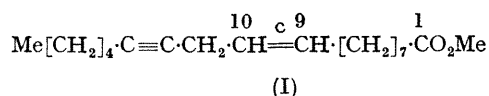


A Route to the Polyacetylenic C₁₈-Acids containing 1-En-4-yne Unsaturation

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Summary A modified Wittig procedure makes possible the synthesis of 1-en-4-yne systems; ethynyl group protection with the trimethylsilyl group facilitates iodoacetylene formation for subsequent coupling reactions.

LABELLED [1,9-¹⁴C, 9-¹⁴C, and 10-³H] methyl crepenynate (I) has been prepared¹ by the route described recently.² Attempts to use an analogous sequence of reactions for the synthesis of the more acetylenic C₁₈ esters (*e.g.* II), postulated to be intermediates in the biogenetic conversion of oleate into some polyacetylenes,³ failed. Two such esters (II and III) have now been prepared in reasonable overall yields (5%) (*cf.* Bohlmann⁴) by the reaction sequence given in the Scheme. This makes possible labelling in a variety of positions, an important requirement for studies of the biogenesis of acetylenic compounds in fungi.



SCHEME

The Wittig reaction failed under normal conditions; it succeeded only when the salt (IV), the aldehyde, and sodium hydride (100%) were stirred together in tetrahydrofuran-dimethyl sulphoxide (3:2) under nitrogen at 0° for 15—50 hr. (similar reaction conditions have been previously employed to prepare $\beta\gamma$ -unsaturated acids⁶). The subsequent cleavage of the silicon-carbon bond was achieved with silver nitrate⁷ (cuprous chloride in aqueous ammonia was also effective) and the resulting silver acetylide was converted into the iodoacetylene (V) which was used in the

coupling reaction. The trimethylsilyl-protected acetylenic phosphonium salt (IV) is likely to be of quite general utility for the synthesis of compounds containing 1-en-4-yne unsaturation.

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