One-step Conversion of Carbonyl Compounds into Acetylenes

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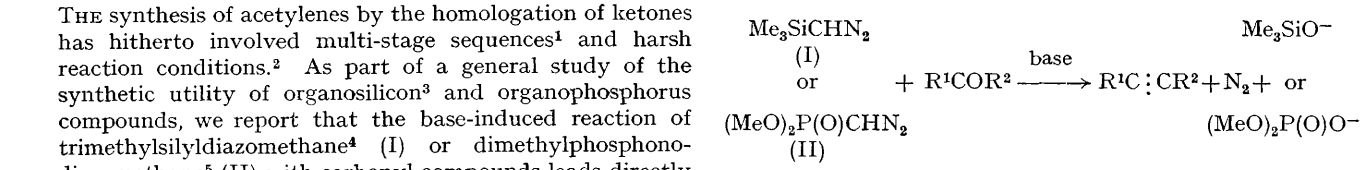
Summary A simple, one-step procedure for the elaboration of ketones and aldehydes into the corresponding homologous acetylenes is presented.

THE synthesis of acetylenes by the homologation of ketones has hitherto involved multi-stage sequences[1] and harsh reaction conditions.[2] As part of a general study of the synthetic utility of organosilicon[3] and organophosphorus compounds, we report that the base-induced reaction of trimethylsilyldiazomethane[4] (I) or dimethylphosphonodiazomethane[5] (II) with carbonyl compounds leads directly to the corresponding homologous acetylenes (Scheme 1).

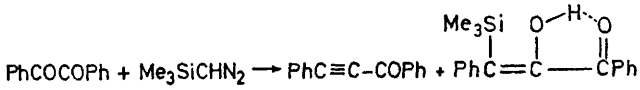
The conditions used are exceptionally mild. For example, (II) (1·1 equiv.) in anhydrous THF at −78° was treated with n-butyl-lithium (1·1 equiv.) in hexane. After 5 min, benzophenone (1 equiv.) in THF was added dropwise, and the cooling bath removed. After 20 h, the reaction was quenched with water; work-up afforded diphenylacetylene (80%), m.p. 60—61°, identical with an authentic sample.



SCHEME 1

With carbonyl compounds possessing α hydrogen atoms, enolisation of the substrate is a competitive reaction: acetophenone is converted into 1-phenylpropyne in 16%

yield, with 50% recovery of starting material. Aldehydes are converted into terminal acetylenes, phenylacetaldehyde giving 3-phenylpropyne in 30% yield.



SCHEME 2

The probable mechanism of this reaction, a Wolff rearrangement followed by oxide elimination, is substantiated by the isolation, in some cases, of the intermediate Wolff product (Scheme 2).

(*Received, 8th January* 1973; *Com.* 028.)

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