Reductive Silylation Reactions of Ethyl 2-Furoates

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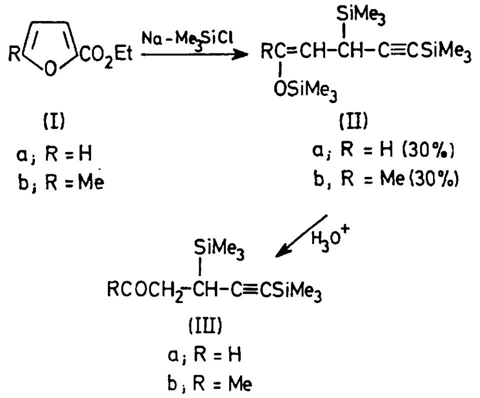
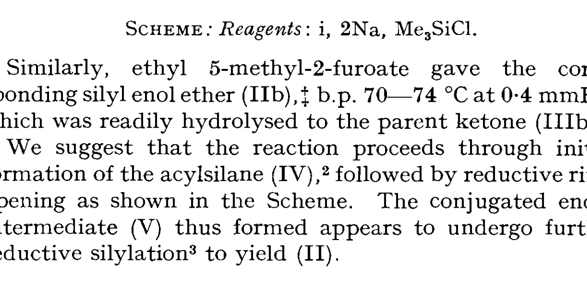
Summary Treatment of ethyl 2-furoate or 5-methyl-2-furoate with metallic sodium in the presence of trimethylchlorosilane affords the trimethylsilyl enol ether of 3,5-bis(trimethylsilyl)pent-4-yn-1-al or 4,6-bis(trimethylsilyl)hex-5-yn-2-one, respectively.

Reductive silylation has introduced a new methodology into synthetic organic chemistry and has offered methods for the ready preparation of various organo-silicon compounds.[1] We have recently described the preparation of 1,1-bis(trimethylsilyl)alkan-1-ols from the corresponding trimethylsilyl carboxylates.[2] We report herein reductive silylation reactions of ethyl furoates, which readily undergo ring-opening to afford versatile reagents for carbon–carbon bond extension.† Thus, treatment of ethyl 2-furoate (Ia) with metallic sodium in the presence of trimethylchlorosilane under reflux in tetrahydrofuran gave the trimethylsilyl enol ether (IIa) of 3,5-bis(trimethylsilyl)pent-4-yn-1-al,‡ b.p. 77—81 °C at 0·5 mmHg, which, upon hydrolysis, afforded the corresponding aldehyde (IIIa),‡ b.p. 118—120 °C at 3 mmHg, quantitatively.





Scheme: *Reagents*: i, 2Na, Me_3SiCl.

Similarly, ethyl 5-methyl-2-furoate gave the corresponding silyl enol ether (IIb),‡ b.p. 70—74 °C at 0·4 mmHg, which was readily hydrolysed to the parent ketone (IIIb).

We suggest that the reaction proceeds through initial formation of the acylsilane (IV),[2] followed by reductive ring-opening as shown in the Scheme. The conjugated enone intermediate (V) thus formed appears to undergo further reductive silylation[3] to yield (II).

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† C–C bond extension reactions by the use of these reagents will be described in the near future.

‡ Satisfactory spectral and analytical data have been obtained for all of these products.

[1] See, for example; K. Ruhlmann, *Synthesis*, 1971, **236**; J. J. Bloomfield, D. C. Owsley, and J. M. Nelke, *Org. Reactions*, 1976, **23**, 259.

[2] I. Kuwajima, T. Sato, N. Minami, and T. Abe, *Tetrahedron Letters*, 1976, 1591.

[3] J. P. Picard, A. Ekouya, J. Dunogues, N. Duffaut, and R. Calas, *J. Organometallic Chem.*, 1975, **93**, 51.