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Regiospecific Addition of Bis(Trimethylsilyl)-Hypophosphite to 2-Halogen-2-Alkenals

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REGIOSPECIFIC ADDITION OF BIS(TRIMETHYLSILYL)-HYPOPHOSPHITE TO 2-HALOGEN-2-ALKENALS

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Abstract 2-Halogen-2-alkenals react regiospecifically with one equivalent of bis(trimethylsilyl)hypophosphite in 1,2-addition mode.

2-Halo-2-alkenals 1 are polydental compounds having two sites of possible nucleophilic attack: β-olefin carbon atom and the carbon atom of the aldehyde group. Recently we have shown that alkenals 1 react with trimethylsilyl derivatives of primary or secondary amines in 1,2- and 1,4-addition mode. On the other hand bis(trimethylsilyl)hypophosphite 2 can react on both the P-H and P-O-Si bonds.²

We have found that bis(trimethylsilyl)hypophosphite 2 reacts easily with aldehydes 1 in 1,2-addition mode only (on the carbonyl group) with the cleavage of the P-O-Si bond. The reaction proceeds regiospecifically irrespectively of both the nature of the halogen atom and the β-substituent in the molecule of initial substrate. The compounds obtained are a mixture of two diastereomers the structure of which is confirmed by ¹H and ³¹P NMR spectroscopy.

$$R' = R = H$$
; $R' = Me$, $R = H$; $R' = Ph$, $R = H$; $R' = R = Ph$; $X = Cl$, Br

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