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PREPARATION AND USE OF 1-IODOALKYL YLIDES

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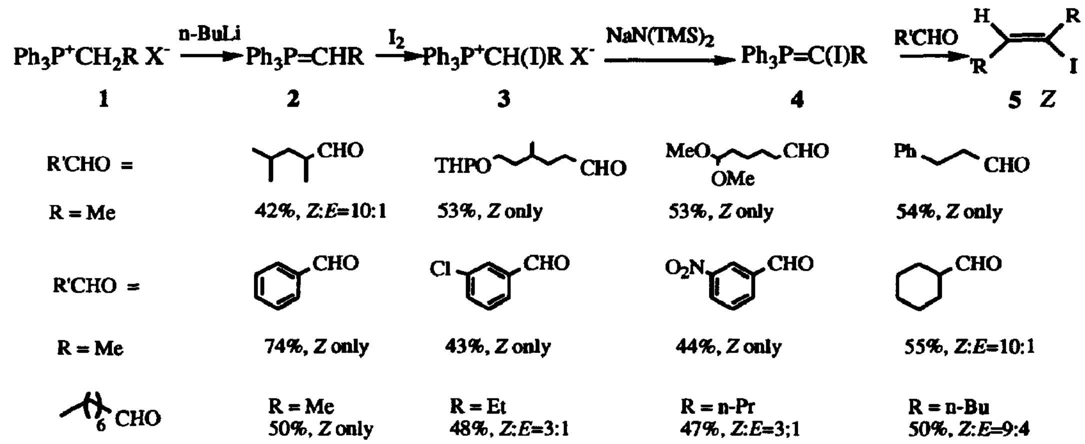
Summary: *α-Iodoalkyl ylides were prepared and used for first time to convert aldehydes to 2-iodo-2-alkenes stereoselectively and to other dialkyl vinyl iodides.*

Many methods have been developed for synthesis of 1-iodo-1-alkenes by routes involving 1-alkyne reduction,[1] but a similar sequence to 2-iodo-2-alkenes from acetylenic precursors has limited application due to difficulties in controlling the regioselective hydrometalation of internal triple bonds.[2] A procedure whereby aldehydes are converted to substituted vinyl iodides would be advantageous and a strategy using the Wittig reaction for preparation of 1-iodo-1-alkenes has been reported.[3] The use of α-carbonyl-stabilized iodo ylides ($Ph_3P=CICO_2R$) has been described,[4] but there is no report on preparation and use of α-iodoalkyl ylides ($Ph_3P=CICH_2R$) for the corresponding iodoalkene construction. We now report a route for conversion of aldehydes to 2-iodo-2-alkenes and other dialkyl iodoolefins recently developed in our laboratory.

To test the feasibility of coupling α-iodoalkyl ylides with aldehydes, we first synthesized reagents **3** by deprotonating compounds **1** with n-butyl lithium and subsequent halogenation of the resulting ylides **2**. It has been reported that "halogenation of strongly basic ylides with free halogen is accompanied by side reactions and is not suitable for preparative application."[4,5] We found that this was the case if iodine was added to ylides **2**, but the inverse addition of **2** to a solution of iodine and tetrahydrofuran at -78 °C provided the desired reagents **3**, which can be isolated as yellowish solids.

Reaction of **3** with sodium hexamethyldisilazane at -20 °C afforded **4**, which reacted with aldehydes to produce the desired iodoolefins **5**. As shown in the Scheme, **1** could be converted to **5** in one pot with similar yields and isomer ratios. Indeed, starting from ethyltriphenylphosphonium salts, 2-iodo-2-alkenes can be prepared stereoselectively. In other cases, two isomers are generally obtained and the stereochemistry depends very little on the reaction conditions. Defining the limits of the method, the synthesis of tetrasubstituted vinyl iodides *via* the Wittig reaction of α-iodophosphoranes with ketones fails.

To our knowledge, this one-pot procedure is the most efficient method known to convert aldehydes to dialkyl vinyl iodides. The reaction conditions are mild and therefore compatible with the synthesis of many types of functionalized vinyl iodides.



a) The *Z*/*E* ratios were determined by NMR and GC/MS, and stereochemistry was assigned by using the products from Na/NH_3 reduction of **5**; see ref. 6. b) Isolated overall yields based on aldehydes.

To a suspension of **1** (X=I, R=Me, 0.84 g, 2.0 mmol) in 10 ml of THF was added at room temperature 1.25 ml of *n*-BuLi (1.6 M) in hexane. After disappearance of the solid material, the solution was transferred to a mixture of iodine (0.45 g, 1.77 mmol) and THF (15 ml) at -78 °C, and the resulting suspension was vigorously stirred for 5 minutes. Sodium hexamethyldisilazane (1.7 ml, 1 M in THF) was added at -20 °C to produce a red solution, followed by stirring for 5 minutes and addition of benzaldehyde (0.17 ml, 1.67 mmol). After reaction for 10 minutes and the usual work up, purification on silica gel gave (Z)-2-iodopropenylbenzene (0.30 g, 74%).

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