

## STEREOSPECIFIC E OLEFINATION OF ALDEHYDES WITH A BISBENZYLIC ARSONIUM YLID-ANION

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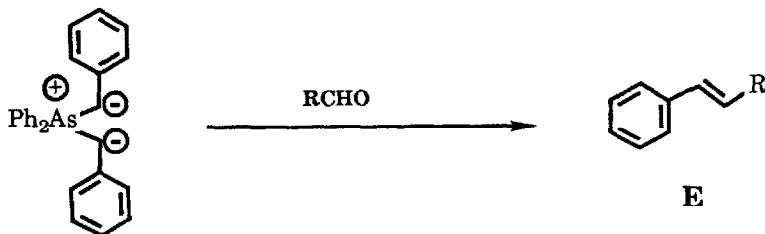
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**Summary:** Stereospecific E olefination of aldehydes with a bisbenzylic arsonium ylid-anion in the presence of HMPA is reported.

Double bond formation via the Wittig reaction is a useful transformation in organic synthesis (1). The stereoselectivity of this reaction for non stabilized ylids can be directed either to the formation of Z olefins under salt free conditions(2) or to the formation of E olefins using DBP (dibenzophospholes) ylids(3). In the case of stabilized ylids high E stereoselectivity can be obtained with arsonium ylids(4).

The low stereochemical control obtained with semi-stabilized ylids(5) prompted us to investigate the reactivity of benzylic ylids in order to specifically form E isomers (Scheme I).

**Scheme I**



Since the pioneer work of Schmidbaur on phosphonium ylid-anions(6), their use in organic synthesis was scarcely investigated until the report of Cristau's group which shows their high reactivity in the Wittig reaction(7).

The recent report of Walker and coll.(8) on the stereochemistry of the reaction

of ylid-anions derived from benzylic ylids with benzaldehyde spurred us to report our own results with this reaction.

Reinvestigation of the reaction in the case of hexanal gave similar results as those reported by Walker. In the presence of HMPA, only small increase of E selectivity is observed after addition of two equivalents of aldehyde, but a significant increase with only one equivalent of aldehyde (Table I).

### Scheme II

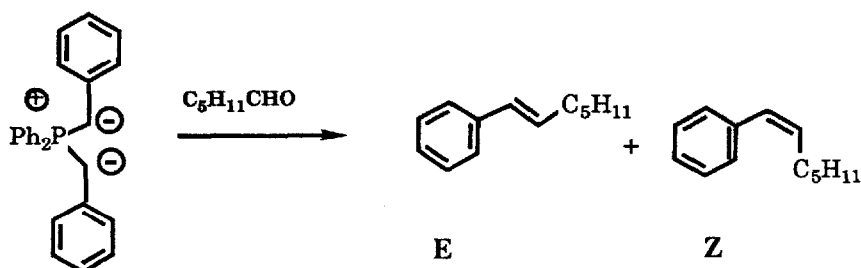


Table I

Eq. nBuLi	Eq. Ald.	Solvent	Temp.	Yield %	E / Z
1	1	THF	RT	85	85/15
1	1	THF	-78°C	85	85/15
2	2	THF	RT	164	93/7
2	1	THF/HMPA*	-78°C	91	95/5
2	2	THF/HMPA*	-78°C	152	96/4

\* 85 / 15: v/v

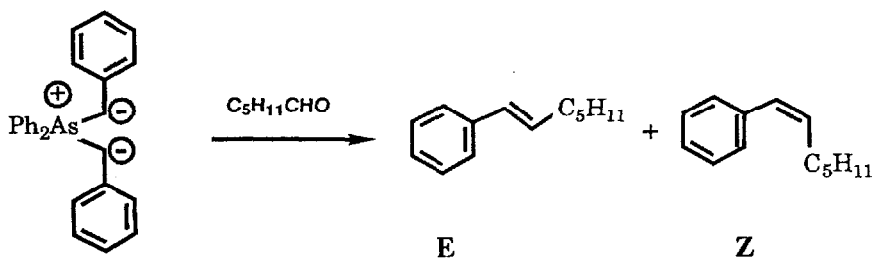
In order to improve the stereoselectivity of this reaction we investigated bisbenzyl arsonium ylid-anions. To our knowledge no arsonium ylid-anions have so far been described in the literature.

The arsonium salt is formed by reacting lithium diphenyl arsenide<sup>(9)</sup> with benzyl bromide in THF at room temperature with subsequent quaternarization of the benzyl diphenyl arsine with benzyl bromide in acetonitrile at room temperature. The ylid-anion is generated after double deprotonation of the salt with two equivalents of

n-butyllithium at  $-40^{\circ}\text{C}$ . After the mixture is stirred for an additional hour at  $-10^{\circ}\text{C}$ . Condensation with hexanal is performed at  $-78^{\circ}\text{C}$ , the reaction mixture is then allowed to warm up to room temperature, and stirred for two additional hours. In THF a complex mixture was obtained whereas in THF/HMPA (85/15) only alkene formation is observed in high yields.

The ylid gives an E/Z ratio of 98/2, whereas with the ylid anion the reaction is stereospecific yielding an E/Z ratio of  $> 99/1$ . No Z isomer could be detected by capillary GC analysis. This was effected by addition of one or two equivalents of aldehyde where only one benzylic group is transferred in contrast to the phosphonium ylid-anions (Table II).

**Scheme III**



**Table II**

Eq. nBuLi	Eq. Ald.	Solvent	Temp.	Yield %	E / Z
2	1	THF	$-30^{\circ}\text{C}$	**	—
2	1	THF	$-78^{\circ}\text{C}$	**	—
2	2	THF	$-78^{\circ}\text{C}$	**	—
1	1	THF/HMPA*	$-78^{\circ}\text{C}$	95	98/2
2	1	THF/HMPA*	$-78^{\circ}\text{C}$	96	$>99/1$
2	2	THF/HMPA*	$-78^{\circ}\text{C}$	91	$>99/1$

\* 85 / 15 v/v

\*\* complex mixture

Arsonium oxide anion formed during the process reacts with n-hexanal but

the  $\beta$ -alkoxy intermediate formed does not react further to form olefins<sup>(10)</sup>.

Currently we are investigating other arsonium ylid-anions to further improve the selectivity in the formation of double bonds.

Notes: All yields are isolated yields and are based on phosphonium or arsonium salt. E/Z ratio were determined by G.C. on a Carlo-Erba SE 54 (25m) at 60°C to 220°C (15°C/mn).

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