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An Easy Access to Symmetrical Z-olefins from Phosphorus Ylides

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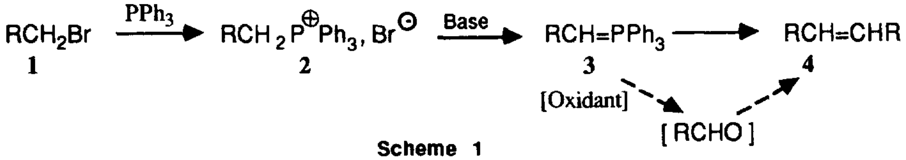
Abstract: Symmetrical Z-olefins are obtained in good to quantitative yields from phosphonium salts *via* an autoxidation process, in salt-free conditions. Copyright © 1996 Published by Elsevier Science Ltd

The Wittig reaction, the reaction of a phosphorus ylide with a carbonyl compound, remains one of the most investigated reactions from both synthetic and mechanistic points of view. However, phosphorus ylides can also afford symmetrical olefins by self-condensation occuring during an autoxidation process. This reaction presumably proceeds *via* the aldehyde (scheme 1):[1]

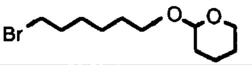
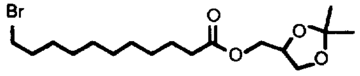


Scheme 1

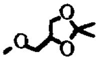
Various oxidants have been proposed[2] and give poor to good yields, depending on the reaction conditions and on the nature of ylides: unstabilized ylides lead to mixtures of *Z* and *E* olefins while stabilized ones give *E* olefins. Pure *Z* selectivity is only observed in case of synthesis of cyclic olefins from bis-ylides[3].

It is well known that the "lithium salt-free" reaction of ylides from triphenylphosphonium salts and NaHMDS with aldehydes predominantly gives Z-olefins[4]. But, to our knowledge, these conditions have not been used for the autoxidation of phosphonium ylides. We wish to report here a simple approach to the synthesis of symmetrical Z-olefins **4** in good to quantitative yields[5]. As shown in **Table 1**, some usual protective groups and various functionalities are compatible with this method. When needed (**2f-g**), 2 eq of NaHMDS are used without loss of selectivity. In the case of stabilized ylide **3h**, the reaction failed[2a,2d] : ethyl acetate and triphenylphosphine oxide were isolated in nearly quantitative yields.

Table 1. Synthesis of Symmetrical Olefins 4 from Bromides 1 *via* Phosphonium Salts 2

Entry	starting bromides 1	product(s) 4	procedure	yield[a] (*Z*/*E*[b])
a	$Br(CH_2)_5CH_3$	$CH_3(CH_2)_4CH{=}CH(CH_2)_4CH_3$	A	96% (96/4)
b	$Br(CH_2)_{10}CO_2Me$	$MeO_2C(CH_2)_9CH{=}CH(CH_2)_9CO_2Me$	A	98% (100/0)
c		$THPO(CH_2)_5CH{=}CH(CH_2)_5OTHP$	A	75% (95/5)
d		$SolkOC(CH_2)_9CH{=}CH(CH_2)_9COSolk$[c]	A	65%[d] (95/5)
e	$Br(CH_2)_8OCONHPh$	$PhNHCO_2(CH_2)_7CH{=}CH(CH_2)_7OCONHPh$	A	45% (95/5)
f	$Br(CH_2)_8OH$	$HO(CH_2)_7CH{=}CH(CH_2)_7OH$	B[e]	85% (95/5)
g	$Br(CH_2)_7CO_2H$	$HO_2C(CH_2)_6CH{=}CH(CH_2)_6CO_2H$	B[e]	91%[f] (96/4)
h	$BrCH_2CO_2Et$	$CH_3CO_2Et + Ph_3PO$	A	0%

a) yields of pure symmetrical olefins. b) +/- 3%; determined by NMR spectroscopy (^1H and ^{13}C)[6,7].

c) Solk:  . d) about 30% of oxidated phosphonium salts were isolated. e) 2 eq of NaHMDS. f) isolated as dimethyl ester after esterification.

The effect of the temperature on yields and on selectivities was examined with the preparation of 9-octadecene **4i** on a 10 mmol scale (scheme 2). It was shown that the Z-selectivity depend slightly on the temperature. Nevertheless, when phosphonium salts are soluble enough, the reaction seems to be better perform at 0°C or less in order to rise the yield (**Table 2**).

$$\underset{\textbf{2i}}{CH_3(CH_2)_8\overset{\oplus}{P}Ph_3,\ \overset{\ominus}{Br}} \longrightarrow \underset{\textbf{4i}}{CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3}$$

Scheme 2

Table 2. Effect of the Temperature on the Synthesis of the 9-octadecene 4i[8]

T(°C)	Yield (%)	Z/E (^{13}C-NMR)	Z/E(GLC)[8]
+ 75	81	91/9	89/11
+25	81	93/7	92/8
0	92	94/6	92/8
-20	98	94/6	94/6

The Z/E selectivity of the Wittig reaction is closely dependent on the salt effects[9]. Lithium salts or any other soluble metal halide affect the final stereoselectivity in two ways depending on the process of the reaction[4a]. We compared quickly some bases with the NaHMDS ("the Rochow base"), in our conditions (Table 3). It was shown that this base is a quite good compromise between a high yield and a good selectivity. It must be pointed out that NaNH$_2$ led surprisingly to very low yields[10]. This appears inconsistent with the usefulness of sodium amide in Wittig reactions[9].

Table 3. Salt effects on the Synthesis of the 9-octadecene 4i

Base	yield	Z/E (^{13}C-NMR)	Z/E(GLC)[8]
(iPr)$_2$NLi	96%	81/19	78/22
NaN(SiMe$_3$)$_2$	81%	91/9	89/11
BuLi	62%	82/18	79/21
NaH	28%	90/10	91/9
NaNH$_2$	9%	n.d.	n.d.
KOH	0%	-	-

In conclusion, we propose a simple useful method to prepare Z-symmetrical olefins from primary alkyl bromides *via* phosphonium salts. This reaction can been of interest to the formation of saturated long chain α,ω- symmetrical compounds, after catalytic hydrogenation.

References and notes

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5. **General procedure:** 0.55 mL of a commercial solution of NaHMDS in THF (2M) were added to a solution of alkyltriphenylphosphonium bromide (1mmol) in 8 mL of dry THF at room temperature. After refluxing for 1h in an open-air system, the mixture is hydrolyzed (NH$_4$Cl sat.), extracted (diethyl ether), dried (MgSO$_4$) and chromatographed on silica gel to afford pure symmetrical olefins (*procedure A*). In case of less soluble phosphonium salts (**2f-g**), a mixture of dry THF and N, N' - dimethylpropyleneurea (DMPU) was conveniently used (*procedure B*).
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8. At least 2 runs for each condition have been performed. For each run, the (Z/E) ratio was determined by gas chromatography (3 injections per run on two columns of different polarity (column BP1 (SGE) and SP-2380 (SUPELCO)). Retention times were compared to those of authentical samples.
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10. Three different samples of sodium amide were used for two different runs, in each case.

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