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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



Various oxidants have been proposed² 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-ylides³.

It is well known that the "lithium salt-free" reaction of ylides from triphenylphosphonium salts and NaHMDS with aldehydes predominantly gives Z-olefins⁴. 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 yields⁵. 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.

Entry	starting bromides 1	product(s) 4	procedure	yield ^{a)} (Z/E ^{b)})
•	Br(CH ₂) ₅ CH ₃	CH ₃ (CH ₂) ₄ CH=CH(CH ₂) ₄ CH ₃	A	96% (96/4)
Ъ	Br(CH ₂) ₁₀ CO ₂ Me	MeO ₂ C(CH ₂) ₉ CH ∝ CH(CH ₂) ₉ CO ₂ Me	A	98% (100/0)
c	Br	THPO(CH ₂) ₅ CH=CH(CH ₂) ₅ OTHP	Α	75% (95/5)
d	" ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	SolkOC(CH ₂)9CH=CH(CH ₂)9COSolk ^{c)}	A	65% ^{d)} (95/5)
e	Br(CH ₂)8OCONHPh	PhNHCO2(CH2)7CH=CH(CH2)7OCONHPh	A	45% (95/5)
1	Br(CH ₂) ₈ OH	HO(CH ₂) ₇ CH=CH(CH ₂) ₇ OH	Be)	85% (95/5)
g	Br(CH ₂)7CO ₂ H	HO ₂ C(CH ₂₎₆ CH=CH(CH ₂)6CO ₂ H	Be)	91% ^{f)} (96/4)
h	BrCH ₂ CO ₂ Et	CH ₃ CO ₂ Et + Ph ₃ PO	A	0%

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

The effect of the temperature on yields and on selectivities was examined with the preparation of 9octadecene **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**).

Table 2. Effect of the Temperature on the Synthesis of the 9-octadecene 4i8

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 effects⁹. 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 NaNH₂ led surprisingly to very low yields¹⁰. This appears inconsistent with the usefulness of sodium amide in Wittig reactions⁹.

Base	yield	Z/E (¹³ C-NMR)	Z/E(GLC) ⁸
(iPr)2NLi	96%	81/19	78/22
NaN(SiMe3)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.
КОН	0%	-	-

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

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

- 1. Bestmann, H.J.; Kratzer, O. Chem. Rev. 1963, 96, 1899-1908.
- a) Bestmann, H.J.; Armsen, R.; Wagner, H. Chem. Ber. 1969, 102, 2259-2269. b) Rihter, B.; Masnovi, J. J. Chem. Soc., Chem. Commun., 1988, 35-37. c) Nürrenbach, A.; Paust, J.; Pommer, H.; Schneider, J.; Schulz, B. Liebigs Ann. Chem., 1977, 1146-1159. d) Bestmann, H. J.; Kisielowski, L.; Distler, W. Angew. Chem. Int. Ed. Engl., 1976, 15, 298-299. e) Nürrenbach, A.; Pommer, H. Liebigs Ann. Chem., 1969, 721, 34-42. f) Davis, F.A.; Chen, B-C. J. Org. Chem. 1990, 55, 360-363.
- a) Bestmann, H.J.; Häberlein, H.; Wagner, H.; Kratzer, O. Chem. Ber. 1966, 99, 2848-2854. b) Bestmann, H.J.; Pfüller, H. Angew. Chem. Int. Ed. Engl. 1972, 11, 508-509.
- a) Schlosser, M; Christmann, K.F. Justus Liebig Ann. Chem. 1967, 708,1. b) Schlosser, M Angew. Chem. Int. Ed. Engl., 1968, 7, 650. c) Schlosser, M; Schaub, B. J. Am. Chem. Soc. 1982, 104, 5821-5823. d) Reitz, A.B.; Mutter, M. S.; Maryanoff, B.E. J. Am. Chem. Soc. 1984, 106, 1873-1875.
- 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 (NH₄Cl sat.), extracted (diethyl ether), dried (MgSO₄) 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*).
- 6. Frost, D.J.; Gunstone, F.D.. Chem. Phys. Lipids 1975, 15, 53-85.

- 7. Gunstone, F.D.; Pollard, M.R.; Scrimgeour, C.M.; Vedanayagam, H.S. Chem. Phys. Lipids 1977, 18, 115-129.
- 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.
- 9. Schlosser, M.; Schaub, B.; de Oliveira-Neto, J.; Jeganathan, S. Chimia 1986, 40, 244-245.
- 10. Three different samples of sodium amide were used for two different runs, in each case.

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