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The Wittig Synthesis of Alkenes under Gas–Liquid Phase-transfer Catalysis

Enrico Angeletti, Pietro Tundo, and Paolo Venturello*
Istituto di Chimica Organica dell'Università, Via G. Bidone 36, 10125 Torino, Italy

Under gas–liquid phase-transfer catalysis conditions, an aldehyde passed in the gaseous state through a solid bed of potassium carbonate and a phosphonium salt, results in the formation of an alkene which is obtained in good yield by condensation and is free from triphenylphosphine oxide, which remains adsorbed on the bed.

Gas–liquid phase-transfer catalysis (g.l.-p.t.c.) has been reported as a method for achieving displacement reactions in which the nucleophilic anion may be added to the reaction or generated by a stronger base.[1]

We report herein the results obtained in the extension of the use of g.l.-p.t.c. and report that Wittig alkene synthesis can be performed, according to equation (1), by passing the aldehyde, in the gaseous state, through a solid bed of the base (K_2CO_3) mixed with a suitable phosphonium salt.

$$\mathrm{Ph_3P^+CH_2R^1X^-\ (solid) + R^2CHO\ (gas)} \xrightarrow[\text{Carbowax 6000(liquid)}]{\mathrm{K_2CO_3(solid)}}$$
$$\mathrm{R^1CH{=}CHR^2\ (gas) + Ph_3P{=}O\ (liquid)} \qquad (1)$$

Table 1. G.l.-p.t.c. synthesis of alkenes [equation (1)].[a,b]

Expt. no.	R^1	R^2	X^-	Carbowax 6000[c]	Temperature/°C	*cis*:*trans*[d] Ratio	Conversion[e] (%)	Yield[f] (%)
1	H	Ph	I	—	170	—	56	47
2	H	Ph	I	+	150	—	98	57
3	Me	Ph	Br	—	170	51:49	20	19
4	Me	Ph	Br	+	150	52:48	77	52
5	Me[g]	Ph	Br	+	150	52:48	100	82
6	$CH{=}CH_2$	Ph	Br	—	170	46:54	14	8
7	$CH{=}CH_2$[h]	Ph	Br	+	150	48:52	90	43
8	$[CH_2]_2Me$[h]	Ph	Br	+	150	67:33	100	86
9[i]	Ph	H	Cl	+	150	—	100	18
10[l]	Ph	Me	Cl	+	150	36:64	96	34
11[l]	Ph	$MeCH_2$	Cl	—	170	37:63	97	57
12	H	$Me[CH_2]_8$	I	—	170	—	95	33
13	H	$Me[CH_2]_8$	I	+	150	—	100	40

[a] 1.0 Mol. equiv. of $Ph_3P^+CH_2R^1X^-$ with respect to R^2CHO, if not otherwise indicated. [b] 0.025 Mol of R^2CHO, if not otherwise indicated. [c] 5% By weight with respect to K_2CO_3 (57 g); — indicates the absence and + the presence of poly(ethylene glycol). [d] By g.l.c. analysis. [e] By ^1H n.m.r., comparing the $-CHO$ signal area to that of the alkenic protons. [f] Established from the weight of collected product, on the basis of the conversion. [g] 1.5 Mol. equiv. with respect to benzaldehyde. [h] 2.0 Mol. equiv. with respect to benzaldehyde. [i] Aldehyde (solid paraformaldehyde was mixed with the reactive bed), 0.125 mol; phosphonium salt, 0.025 mol. [l] Aldehyde, 0.075 mol; phosphonium salt, 0.025 mol.

In the Wittig reaction, either carried out under classical conditions,[2] or under liquid–liquid (l.l.[3]) or solid–liquid (s.l.[4]) p.t.c. conditions, separation of the alkene from triphenylphosphine oxide is always necessary and often requires careful chromatography. In this connection alkyltriphenylphosphonium salts were immobilised on polymeric supports in order to achieve complete elimination of all the phosphorus-containing species with the removal of the polymer at the end of the reaction.[5]

Under g.l.-p.t.c. conditions the reaction is carried out in a thermostatted reactor containing solid K_2CO_3 finely powdered and mixed with a suitable phosphonium salt. The aldehyde is passed (using a peristaltic pump) through the solid bed where the temperature (150—170 °C) and the pressure (15 Torr) guarantee that both the reacting carbonyl compound and the alkene produced are gaseous. The product is condensed by cooling at the reactor outlet (product collection begins 5—10 min after the entrance of the aldehyde; reaction temperature and pressure are maintained for *ca.* 20 min so that all the alkene is recovered); the high-boiling triphenylphosphine oxide remains in the reactor.†

The results obtained with different aldehydes and different alkyltriphenylphosphonium salts are reported in Table 1.

The Wittig synthesis did not produce alkenes under l.l.- and s.l.-p.t.c. conditions,[3b] or under g.l.-p.t.c. conditions if a ketone was used as the carbonyl compound. However, a wide range of aldehydes can be used: aliphatic aldehydes, even the water soluble ones, *e.g.* formaldehyde, acetaldehyde, and propionaldehyde give good results as the reaction was conducted in the absence of water. Aromatic aldehydes bearing hydrolysable groups can be used in the reaction (*e.g.* $4\text{-}MeCO_2C_6H_4CHO$, not reported in Table 1, was transformed into $4\text{-}MeCO_2C_6H_4CH{=}CH_2$ in 10% yield, without loss of the ester group).

Under the reported conditions, in the absence of any interaction with polar protic solvents, potassium carbonate was basic enough to generate the ylide even from the less acidic phosphonium salts (*e.g.* butyltriphenylphosphonium bromide and ethyltriphenylphosphonium bromide).

Particular attention must be paid to the reaction temperature, as the phosphonium salts, particularly the highly reactive ones, partially decompose at 170 °C before they can react with the aldehyde.

The main features that make this method a viable alternative to those hitherto reported for alkene synthesis, can be summarized as follows: (i) the alkene is produced quickly and is free from unreacted aldehyde if an excess of phosphonium salt (1.5—2.0 mol. equiv. with respect to the aldehyde) is used; (ii) neither aqueous nor organic solvents are used; and (iii) possible polymerization by-products remain in the reactor with triphenylphosphine oxide which can easily be recovered.

As regards the mechanistic aspects of reaction (1), on the basis of previously reported results under g.l.-p.t.c. conditions, a liquid film through which the aldehyde diffuses and reacts would appear to be necessary.[6] In this case the nature of such a liquid phase is not at present well defined and is under study: it may contain the ylide, the phosphonium salt having the carbonate as counterion, triphenylphosphine oxide, or a eutectic mixture.‡ The importance of the liquid phase, however, is confirmed by the fact that poly(ethylene glycol)–Carbowax 6000 increases both the amount of conversion and the yield of the reaction; in the molten state it provides the liquid film that can dissolve the phosphonium salt and/or the ylide thus offering a more effective reaction medium to the aldehyde as it diffuses through it.

The *cis*:*trans* ratios reported in Table 1 seem to follow

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† In a typical experiment, Carbowax 6000 (3.0 g) was dissolved in methanol, the K_2CO_3 (57.0 g) was added, and the solvent was removed under vacuum. The resulting solid mass was oven-dried at 150 °C for 5 h and successively mixed and powdered with ethyltriphenylphosphonium bromide (0.0375 mol, 13.9 g). The reactive bed was introduced into a double-jacket glass column (volume 115 ml, length 40 cm) thermostatted at 150 °C; benzaldehyde (0.025 mol, 2.5 ml) was introduced into the column with the aid of a peristaltic pump at a flow rate of 1.5 ml min^{-1}. β-Methylstyrene (2.4 g) was collected at the column outlet by condensation within 30 min. During the synthesis the apparatus was kept under vacuum (15 Torr). The reaction mixture was analysed by ^1H n.m.r. spectroscopy for conversion (100% conversion, 82% yield) and by i.r. spectroscopy and g.l.c. to estimate the *cis*:*trans* ratio. To recover $Ph_3P{=}O$, the bed was extracted with diethyl ether in a Soxhlet apparatus for 5 h; evaporation of the solvent gave a yield of triphenylphosphine oxide (5.2 g, m.p. 157 °C) approximately corresponding to the amount of reacted benzaldehyde.

‡ The m.p. of all the alkyltriphenylphosphonium halides used was higher than the reaction temperature.

the trend previously established;[7] resonance-stabilized ylides gave predominantly *trans*-alkenes (expt. 6, 7, and 9—11), while the reactions with non-stabilized ylides gave a slight prevalence of *cis*-products (exp. 3—5 and 8).

The reaction did not afford isomerization by-products: undec-1-ene was the only reaction product from decanal (expt. 12, 13); the collected β-methylstyrene (expt. 5) was passed over the same exhausted bed and neither product loss nor change in the *cis*: *trans* ratio were detected, thus showing that no polymerization or isomerization reactions took place after the collapse of the betaine to give the alkene.

We are now turning our attention to the possibility of introducing the carbon–carbon double bond in a stereoselective manner by changing the nature of the solid base and the catalyst and consequently the reaction micro-environment.

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