Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Unusual temperature dependence of salt effects for "on water" Wittig reaction: hydrophobicity at the interface

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Supporting Information

Materials:

The aldehydes **1a-d** were freshly distilled prior to their use. All commercially available salts – NaCl, LiCl and GdnCl were dried under vacuum for 6 h.

Synthesis of (ethoxymethylene)triphenylphosphorane (2):

Triphenylphosphine (1.049 g, 4 mmol) was stirred in 50 mL water. Ethylbromoacetate (0.751 g, 4.5 mmol) was added dropwise to the suspension. The resultant solution was stirred for 30 min. at room temperature to give (ethoxymethylene) triphenylphosphonium bromide. The reaction mixture was then washed with ether to remove the unreacted starting materials. Dilute NaOH solution was added dropwise till complete precipitation of the ylide was observed. The precipitate was filtered and washed till neutral to give (ethoxymethylene)triphenylphosphorane. ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.7-7.3 (m, 15H), 3.94 (q, 2H, J_{HH}= 7.0 Hz, CH$_2$), 3.34 (br, 1H), 0.92 (t, 3H, J_{HH}= 7.0 Hz, CH$_3$); {lit.: ^{1}H NMR δ 8.0-7.3 (m), 3.99 (q, J_{HH}= 7.0 Hz, CH$_2$), 2.91 (br, CH), 1.07 (t, J_{HH}= 7.0 Hz, CH$_3$)}[1]

The isolated yield for the reaction of **1a** with **2** carried out in water at 298.15 K was ~ 90% in 1 h. The purity of the product was determined using NMR spectroscopy. This confirmed that the aldehyde was principally consumed by the Wittig reaction (and not by any other side reaction). Thus, the change in concentration of the aldehyde can be treated as a reliable indicator of the reaction progress.

It was observed that the reaction proceeded to near completion in almost all the cases. The yields and the E/ Z selectivities are reported in Table 1.

Table 1: Yields and E/Z selectivities for the Wittig reaction of **1a** with **2** in different media at 298 K.

| Reaction medium	Yield (%)^a	E/Z ratio^b
Methanol	95	75:25
Water	92	93:7
2 M LiCl	89	91:9
2 M NaCl	89	91:9
2 M GnCl	71	82:18
2 M LiClO$_4$	84	83:17

^{a} Isolated yields, after a reaction time of 3 h.

^{b} Determined from NMR spectra of the crude product mixture. The results are in agreement with the values reported in literature.[2]
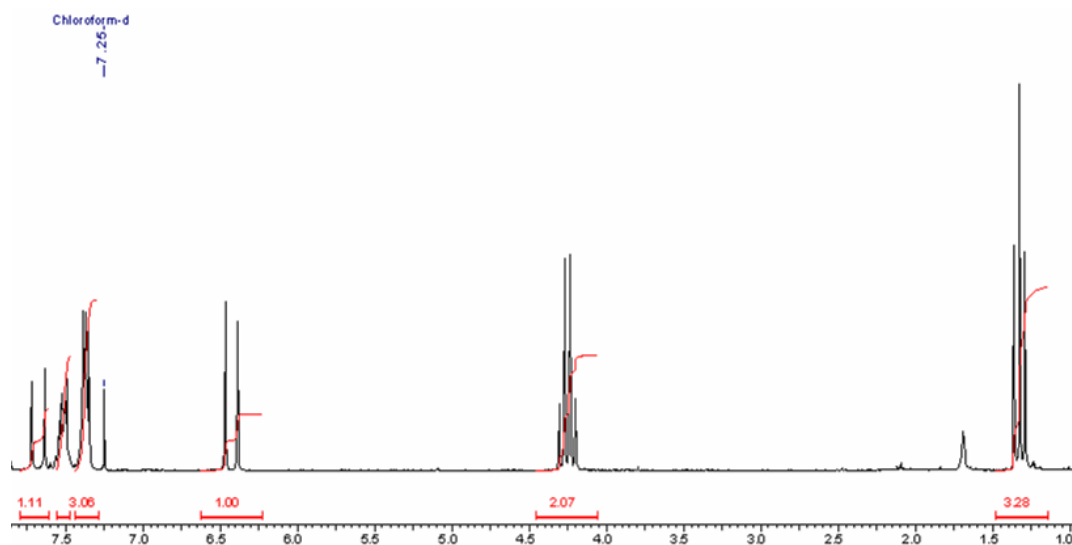
NMR Spectra:

^{1}H NMR of (ethoxymethylene)triphenylphosphorane, **2**

Solvent: CDCl$_3$
200 MHz
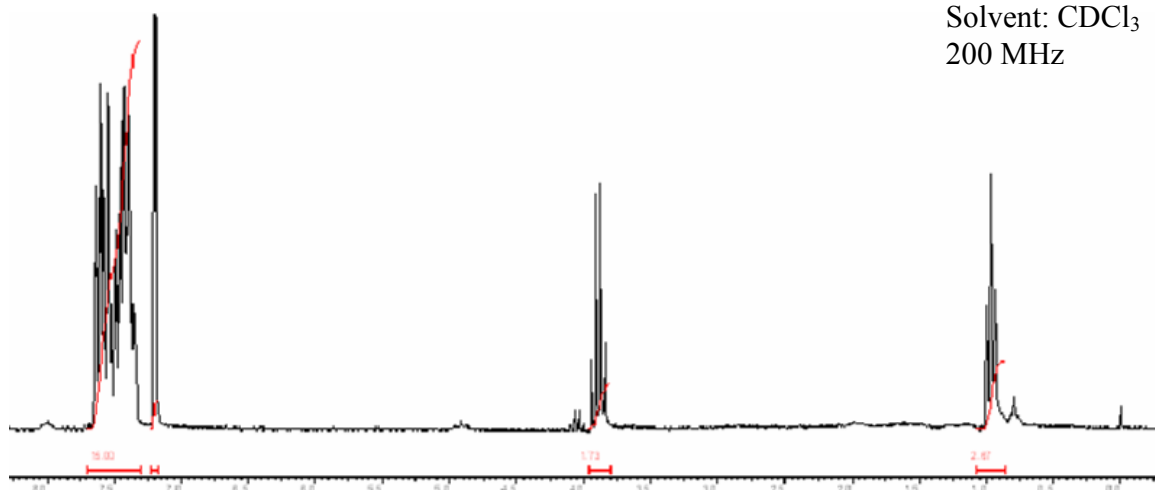
^{1}H NMR of ethylcinnamate, Wittig product of the reaction **1a** + **2**

Solvent: CDCl$_3$
200 MHz

Kinetic Analysis:

For a standard kinetic run, the 1mM aldehyde solution (1 μmol in 10 mL) was allowed to equilibrate, using a constant temperature water bath (precision ± 0.01 K) at the desired temperature for at least 30 min. The reaction was initiated by addition of **2** (5 μmol in 10 mL) into the above aldehyde solution. The resulting heterogeneous mixture was stirred vigorously to prevent aggregation of solid ylide particles. At regular intervals, 100 μL aliquots were withdrawn for their analysis. The reaction was quenched using 0.2 M HCl. The reaction progress was monitored by following the decrease of the aldehyde concentration using UV spectrophotometry.
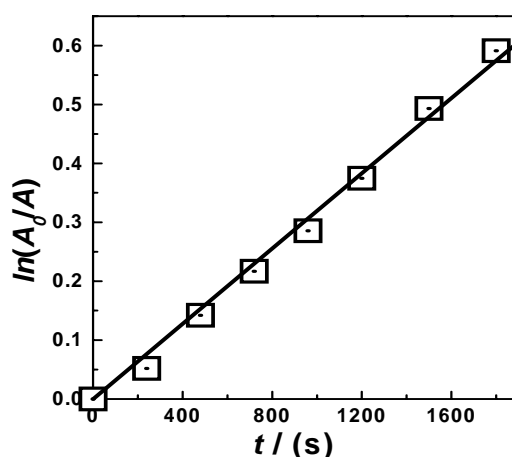
Plot of $\ln(A_0/A)$ against time, t for the Wittig reaction of **1a** with **2** in water at 298.15K

The amount of aldehyde in the solution was estimated by conversion to the hydrazone derivative by addition of 5×10^{-3} M methanolic solution of 2,4-dinitrophenylhydrazine.[3] On addition of 5% KOH, the hydrazone derivative gave a bright red colouration, the absorbance of which was measured spectrophotometrically.

The change in absorbance due to change in concentration of the aldehyde was measured. The plot of $\ln(A_0/A)$ against time gave a straight line of gradient k, the pseudo-first order rate constant (correlation coefficient, $R > 0.98$). The rate constant thus obtained is, in fact, an apparent rate constant since the reaction mixture was heterogeneous in nature. The rate constants were reproducible within $\pm$ 3 % at 298.15 K and $\pm$ 6 % at 338.15 K.

Homogeneous and heterogeneous kinetic analysis:.

For the reaction of **1a** with **2** in homogeneous conditions, a 1.25 mM stock solution of the ylide **2** was prepared by overnight stirring. 8 mL of the solution was equilibrated at 298 K for 30 min. The reaction was initiated by addition of 2 mL of temperature-equilibrated 5 mM solution of **1a** to result in a final concentration of 1 mM for the aldehyde and the ylide each. The progress was monitored by taking aliquots at regular intervals.

The homogeneous run was compared to the heterogeneous reaction in which 10 mL of the appropriately diluted aldehyde solution was equilibrated at the required temperature. The reaction was initiated in this case by the addition of solid ylide to result in suspension of ylide particles. The amount of aldehyde and ylide present in the reaction mixture in both the cases was identical.

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2. A. El-Batta, C. Jiang, W. Zhao, R. Anness, A. L. Cooksy andM. Bergdahl, *J. Org. Chem.*, 2007, **72**, 5244.
3. A. I. Vogel, *Vogel's Textbook of Quantitative Chemical Analysis*; 5th Ed. G. H. Jeffery, J. Bassett, J. Mendham, R. C. Denney, Eds.; ELBS-Longman, UK, **1989**, p. 706.