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Preliminary Communication

[2,3]-Wittig rearrangement in the α-allyloxy methylphosphonate series

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Abstract

The treatment of some diethyl (α-allyloxymethyl)phosphonates with two equivalents of lithium diisopropylamide at −70°C in THF led, after hydrolysis, to the corresponding (α-hydroxy-α-allylmethyl)phosphonates resulting of [2,3]-Wittig rearrangement of α-metallated starting phosphonates.

Key words: Phosphonate; Allyloxy

The [2,3]-sigmatropic rearrangement (Scheme 1) of conjugate bases of allylic-type ethers **I** into the β,γ-unsaturated alkoxides **II**, called the [2,3]-Wittig rearrangement, is a well-documented process, which has found many useful applications, particularly in the field of stereocontrolled synthesis [1–4].

To the best of our knowledge, numerous functional groups G have been used with a view to stabilizing the α-oxycarbanion **I**, including aryl, alkenyl or alkynyl moieties, and carboxylic acid derivatives but not phosphonate groups. On the other hand, however, carbanions of α-oxyalkyl-phosphonates have received much attention as Horner–Emmons reagents for aldehyde homologations [5–7].

In connection with our work on the use of α-lithioalkylphosphonates as functional group carriers [8–10], we tried to generate carbanion **2a** by treating (α-allyloxymethyl)phosphonate **1a** with lithium diisopropylamide (LDA) in THF at −70°C. ^{31}P-NMR analysis of hydrolyzed samples of the reaction mixture revealed a quantitative formation of carbinol **4a** after 2 h at −70°C. With a view to generalizing this result, we decided to examine the behaviour of some other (α-allyloxymethyl)phosphonates **1** under the same conditions. The results are reported in Scheme 2.

From our observations we draw the following conclusions.

The transformation of **1** into **3** is slow at −70°C (2 h for **1a** and **1b**, 3.5 h for **1c** and 4 h for **1d**); lengthening the time of the reaction for assays **c** or **d** did not increase the amount of transformation.

The overall process is equilibrated and sensitive to steric requirements: the reaction was nearly quantitative for **1a** and **1b** but incomplete for **1c** (90%) and **1d** (50%), as determined by ^{31}P NMR analysis of crude mixtures, after hydrolysis. These best results were obtained in the presence of two equivalents of LDA. The use of only one equivalent of base decreased the yields of carbinols **4** (for example, the degree of transformation of **1a** dropped to 10%), whereas the use of a larger excess (3 equiv.) gave complex mixtures. Likewise, raising the temperature of metallation above −70°C led to several unidentified by-products.

The yield of isolated carbinol **4** was enhanced when the reaction mixture was rapidly quenched at −70°C with the minimum quantity of aqueous acidic solution. These precautions reduced the loss of carbinol due to its easy cleavage in aqueous basic medium [11,12], and from its solubility in water. Moreover, carbinols **4** exhibit some sensitivity to distillation and were better purified by column chromatography over silica-gel.

As proved by ^{31}P NMR spectroscopy, crude carbinols **4b** and **4c** were obtained as mixtures of diastereoisomers in ratio of 95/5 (21.8 ppm/21.6 ppm) for **4b** and of 50/50 (22.7 ppm/22.6 ppm) for **4c**. During purification of **4b**, the major diastereoisomer was isolated pure.

In a typical procedure, to a stirred 1.6 M solution of Li^{n}Bu in hexane (12.5 ml, 20 mmol) at −20°C, di-isopropylamine (2 g, 20 mmol) in THF (15 ml) was added dropwise. After 15 min, the mixture was cooled down to −70°C and diethyl (allyloxymethyl)phosphonate **1a** (2.08 g, 10 mmol) in THF (10 ml) was slowly dropped at −70°C. Stirring was continued at −70°C, while reaction progress was monitored by ^{31}P NMR analysis of hydrolyzed samples: no starting phosphonate **1a** (20.3 ppm in $CDCl_3$) was detected after about 2 h. The mixture was hydrolyzed at −70°C with aqueous 4 M HCl solution (5.5 ml), diluted with diethylether (20 ml) and warmed to room temperature. The organic layer

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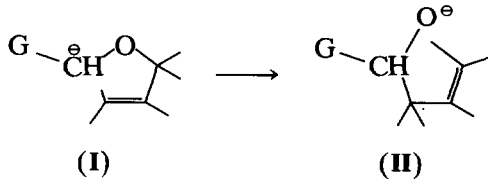
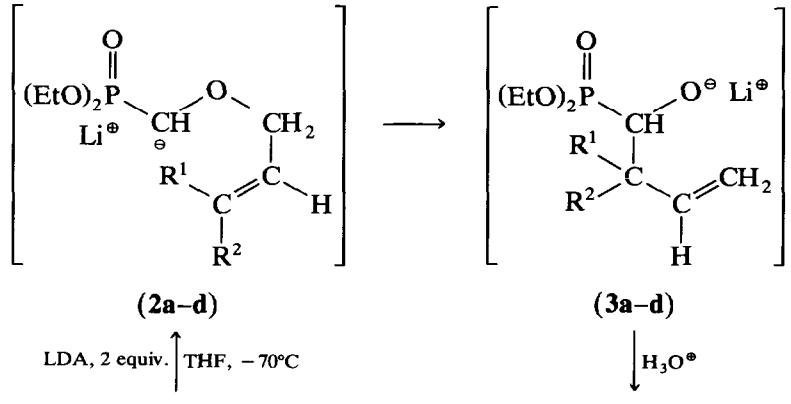


(I) (II)

Scheme 1.

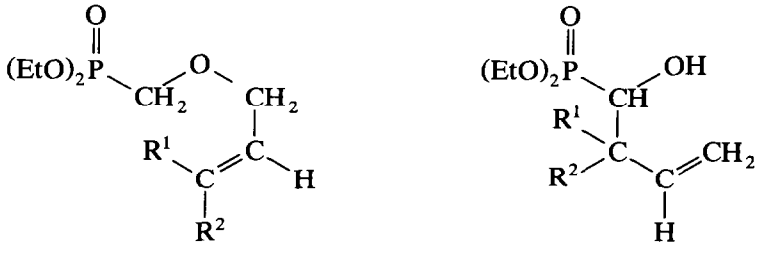
was rapidly decanted and separated; the aqueous layer was extracted with dichloromethane (3 × 20 ml) and the combined organic layers were dried ($MgSO_4$). The solvent was removed under reduced pressure giving the crude product which exhibited a single signal in ^{31}P NMR spectrum (22.9 ppm in $CDCl_3$). The crude oil was purified by chromatography over SiO_2 (eluent: diethylether) affording pure carbinol **4a** as a pale-yellow oil (1.5 g, 7.2 mmol, 72% yield). ^1H NMR (200 MHz, $CDCl_3$, δ in ppm): 1.35 (t, $J = 7.5$ Hz) 6H ($2 \times CH_3CH_2O$), 2.3 to 2.7 m 2H ($CH_2CH{=}CH_2$), 2.9 lb 1H (O*H*), 3.8 to 4.0 m 1H (C*H*OH), 4.2 (qui, $J = 7.5$ Hz) 4H ($2 \times OCH_2CH_3$), 5.1 to 5.3 m 2H ($CH_2{=}CH$), 5.8 to 6.1 m 1H ($CH{=}CH_2$).

A procedure similar to the one above was used for the preparation and isolation of **4b–d**. **4b** (68% yield), major diastereoisomer isolated (^{31}P NMR, $\delta = 21.8$ ppm in $CDCl_3$) as a white solid (M.p. = 97°C); ^1H NMR ($CDCl_3$, δ in ppm): 1.1 to 1.3 m 6H ($2 \times CH_3CH_2O$), 2.6 lb 1H (O*H*), 3.7 to 4.3 m 6H ($2 \times OCH_2CH_3$, C*H*OH, CHC_6H_5), 5.1 to 5.3 m 2H ($CH_2{=}CH$), 6.1 to 6.3 m 1H ($CH{=}CH_2$), 7.3 to 7.4 s 5H (C_6H_5). **4c** (60% yield) isolated as a pale-yellow oily mixture of two diastereoisomers (^{31}P NMR, $\delta =$ 22.7 and 22.6 ppm in $CDCl_3$, ratio = 1/1); ^1H NMR ($CDCl_3$, δ in ppm): 1.15 (d, $J = 6.5$ Hz) 3H (CH_3CH),



(2a–d) (3a–d)

LDA, 2 equiv. ↑ THF, −70°C ↓ $H_3O^{\oplus}$



(1a–d) (4a–d)

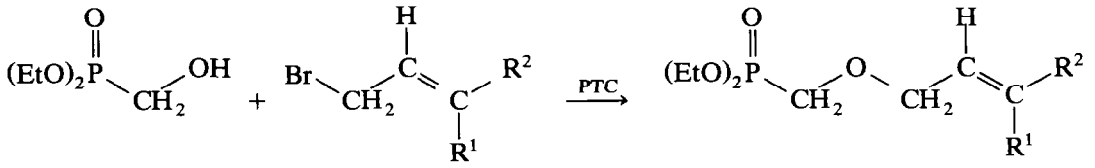
	R^1	R^2
a	H	H
b	H	Ph
c	H	Me
d	Me	Me

	^{31}P NMR δ (ppm) *	Isolated Yield (%) **
a	22.9	72
b	21.8 & 21.6	68
c	22.7 & 22.6	60
d	22.3	28

* In $CDCl_3$

** Purified by column chromatography

Scheme 2.



(5) (6a–d) (1a–d)

Scheme 3.

1.2 to 1.4 (t, $J = 7.5$ Hz) 6H ($2 \times CH_3CH_2O$), 2.5 to 2.7 m 1H ($CHCH_3$), 3.4 lb 1H (OH), 3.6 to 3.9 m 1H ($CHOH$), 4.0 to 4.2 m 4H ($2 \times OCH_2CH_3$), 4.9 to 5.2 m 2H (CH_2=CH), 5.7 to 6.0 m 1H (CH=CH_2). **4d** (28% yield) isolated as a pale-yellow oil; ^{1}H NMR ($CDCl_3$, δ in ppm); 1.15 d 6H ($2 \times CH_3C$), 1.3 (t, $J = 7.5$ Hz) 6H ($2 \times CH_3CH_2O$), 2.7 lb 1H (OH), 3.6 (d, $J = 8$ Hz) 1H ($CHOH$), 4.0 to 4.2 m 4H ($2 \times OCH_2CH_3$), 5.0 to 5.2 m 2H (CH_2=CH), 5.9 to 6.1 m 1H (CH=CH_2).

The starting phosphonates **1** were prepared from diethyl (α-hydroxymethyl)phosphonate **5** [13] and commercially available allyl bromides **6** under liquid-liquid phase transfer catalysis (PTC) conditions (Scheme 3) and purified by distillation (yields (%): **1a** (63%), **1b** (72%), **1c** (54%), **1d** (61%)).

Work is in progress on some synthetic applications of this rearrangement and its possible extension [14*].

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14 The extension of this work is being carried out in collaboration with S. Masson and coworkers at the University of Caen, France.