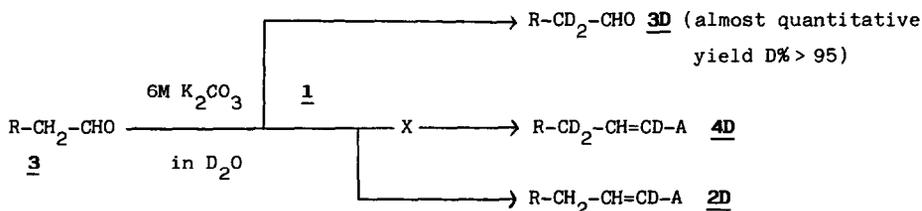


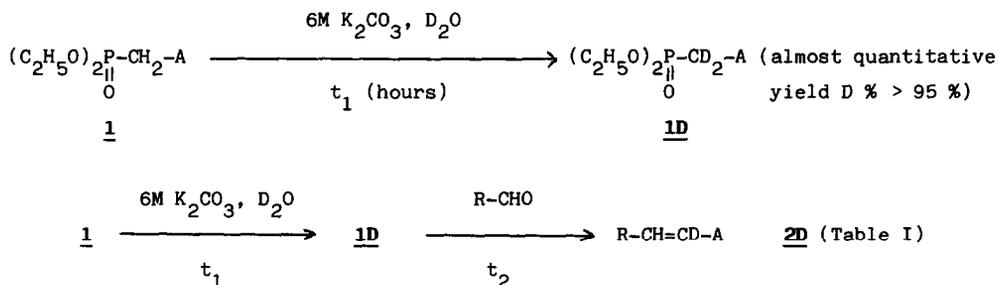
phosphonates	$(\text{EtO})_2\text{P}(\text{CH}_2)_2\text{CH}$	$(\text{EtO})_2\text{P}(\text{CH}_2)_2\text{CO}_2\text{Et}$	$(\text{EtO})_2\text{P}(\text{CH}_2)_2\text{CO-CH}_3$	$(\text{EtO})_2\text{P}(\text{CH}_2)_2\text{CH-EN}$	$(\text{EtO})_2\text{P}(\text{CH}_2)_2\text{CO}_2\text{Et}$	$(\text{EtO})_2\text{P}(\text{CH}_2)_2\text{CO-CH}_3$
aldehydes	$\text{C}_6\text{H}_5\text{-CHO}$	$\text{C}_6\text{H}_5\text{-CHO}$	$\text{C}_6\text{H}_5\text{-CHO}$	$\text{CH}_3(\text{CH}_2)_5\text{-CHO}$	$\text{CH}_3(\text{CH}_2)_5\text{-CHO}$	$\text{CH}_3(\text{CH}_2)_5\text{-CHO}$
Mode	t A(7H) B(3H/5H) t_1/t_2	-	-	-	-	-
Yields %	97	95	90	97	99	90
Deuterium Incorporation % on 2 position	95	> 95	90	> 95	> 95	95
Stereoselectivity ϵ/Z	2/1	2/1	100/0	2/1	2/1	100/0
Products	$\text{C}_6\text{H}_5\text{-CH=CD-CN}$ 1 2 3	$\text{C}_6\text{H}_5\text{-CH=CD-CO}_2\text{Et}$ 1 2 3	$\text{C}_6\text{H}_5\text{-CH=CD-C-CH}_3$ 1 2 3	$\text{CH}_3(\text{CH}_2)_4\text{-CH}_2\text{-CH=CD-CN}$ 4 1 2 3	$\text{CH}_3(\text{CH}_2)_4\text{-CH}_2\text{-CH=CD-CO}_2\text{Et}$ 4 2 1 2 3	$\text{CH}_3(\text{CH}_2)_4\text{-CH}_2\text{-CH=CD-C-CH}_3$ 4 2 1 2 3
B-R(νc)/cmHg.	86/1	68/0.06	58/0.3	44/0.1	49/01	45/0.1
MS	$M^+ = 130$	$M^+ = 177$	$M^+ = 147$	$M^+ = 140$	$M^+ = 185$	$M^+ = 155$
^1H NMR ppm CDCl_3/TMS	1 7.80	1 6.40	1 6.45	4 2.95 m 1 6.70 t	4 2.25 m 1 7.05 t	4 2.35 m 1 6.95 t
^{13}C NMR ppm CDCl_3/TMS	1 150.2(E) 2 148.5(Z) 3 95.8 118.0	1 144.4 2 118.0 3 166.65	1 143.9 2 118.0 3 180.7	4 28.85 1 156.0(E) 155.0(Z) 2 99.7 3 117.5(E) 116.0(Z)	4 29.1 1 149.0 2 121.3 3 166.5	4 29.05 1 149.3 2 121.4 3 180.3
^2D NMR ppm CDCl_3/TMS	2 6.10	2 5.40	2 6.15	2 5.50	2 5.65	2 6.20

Analytical data (particularly isotopic analyses) were obtained from ^1H (90 MHz), ^2D and ^{13}C (22.5 MHz) N.M.R. and mass spectroscopy. The stereochemistry was identical for both labelled and non labelled olefins.

Although total deuteration (> 95 %) of methylene groups of aliphatic aldehydes can be performed in the presence of a 6M $\text{K}_2\text{CO}_3\text{-D}_2\text{O}$ solution, no deuteration was observed in this position in the presence of phosphonates (absence of **4D**), since the WITTIG-HORNER reaction proceeds faster (Mode A).

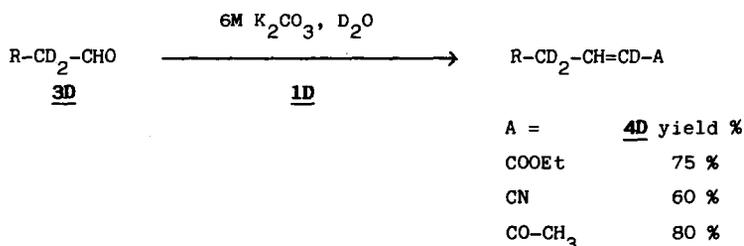


"Labelling improvement" is achieved (% D > 95 %) using a *two-step one-pot* procedure (mode B) in which the carbonyl compound is added a few hours (t_1) after **1** in order to form the deuterated phosphonate **1D** before the WITTIG-HORNER reaction occurs. α,α -dideuterated phosphonate **1D** can be prepared and isolated almost quantitatively (% D on methylene > 95 %) after shaking for t_1 hours.

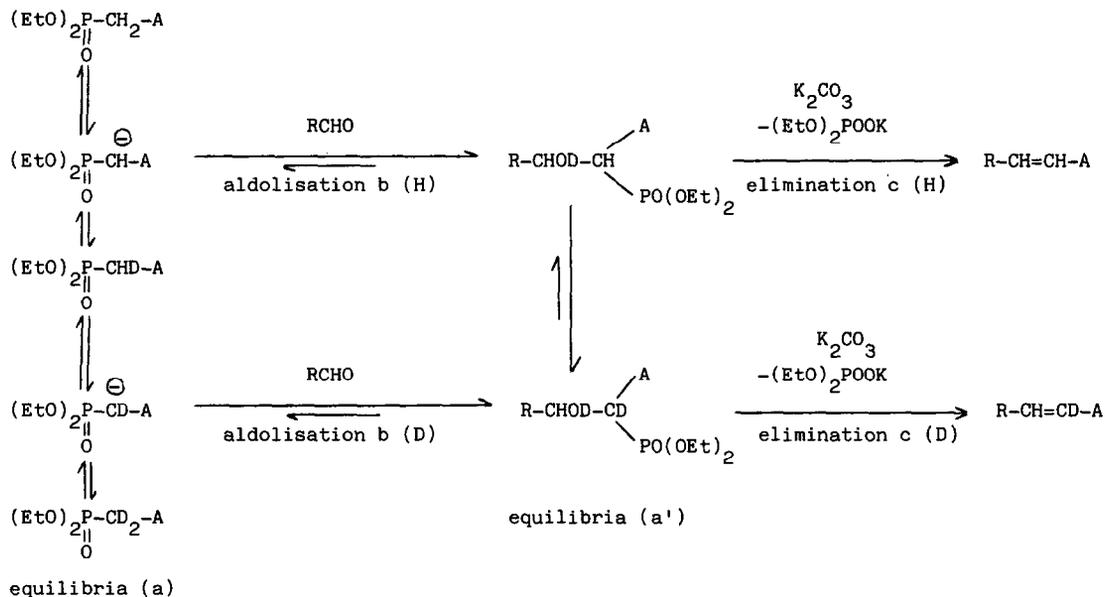


It can be expected that the WITTIG-HORNER reaction of freshly distilled α,α -dideuterated phosphonate **1D** with an aldehyde in the presence of a new 6M $\text{K}_2\text{CO}_3\text{-D}_2\text{O}$ solution would improve the labelling (*two-step two-pot* procedure). However the results obtained using mode B for A = COOEt, CN or CO-CH₃ in **1** and benzaldehyde or heptanaldehyde show that it is not absolutely necessary (see Table I) (**10**).

The WITTIG-HORNER reaction of **3D** using the latter procedure gives rise to **4** in high yield.



Results concerning the WITTIG reaction under almost identical conditions are now available.



SCHEME : WITTIG HORNER Reaction in D_2O/K_2CO_3

REFERENCES

- 1 - M. GRAFF, A. AL DILAIMI, P. SEGUINEAU, M. RAMBAUD, J. VILLIERAS, *Tetrahedron Lett.*, **27**, 1577 (1986).
- 2 - J. VILLIERAS, M. RAMBAUD, *Synthesis*, 300 (1983).
- 3 - J. VILLIERAS, M. RAMBAUD, *C.R. Acad. Sc. Paris, Série II*, **296**, 1175 (1983).
- 4 - M. RAMBAUD, A. DeI VECCHIO, J. VILLIERAS, *Synthetic Comm.*, **14**, 833 (1984).
- 5 - J. VILLIERAS, M. RAMBAUD, *Synthesis*, 924 (1982).
- 6 - J.L. BELLETIRE, *Synthetic Comm.*, **13**, 589 (1983).
- 7 - A.B. REITZ, B.E. MARYANOFF, *Synthetic Comm.*, **13**, 845 (1983).
- 8 - D. BEEMAN, C. WENGER, H.D. PERLMUTTER, *Synthetic Comm.*, **13**, 853 (1983).
- 9 - M. ORFANOPOULOS, *J. Chem. Res.*, **5**, 188 (1982).
- 10 - General procedure, mode B (for mode A, $t_1 = 0$ and $t_2 = t$). Dry potassium carbonate (6.5 g, 45 mmoles), deuterium oxide (7 ml) and triethylphosphonoacetate (3.3 g, 15 mmoles) are stirred vigorously in a dry flask for 20 hours at room temperature under nitrogen atmosphere. Benzaldehyde (1.65 g, 15 mmoles) is then introduced and stirring is continued for 24 hours. Extraction (diethylether, 20 ml x 3) is performed after addition of water (H_2O , 10 ml). After usual treatment 2D-cinnamaldehyde (2.63 g, yield = 97 %, D % > 95 %) is obtained by distillation (B.P. = 68°C/0.06 mmHg).

(Received in France 12 October 1987)