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FLUORIDE ION INDUCED TERMINAL OLEFIN SYNTHESIS FROM β-HYDROXYALKYLPHOSPHONATES

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β-Hydroxyalkylphosphonates, prepared readily from alkylphosphonates and carbonyl compounds, were treated with a fluoride ion to give the corresponding olefins in fairly good yields. Use of CsF in N,N-dimethylformamide gave the best result.

Horner-Emmons reactions of alkylphosphonates with a carbanion stabilizing α-substituent have been often utilized as a key step for the synthesis of natural products.[1] However, alkylphosphonates without any stabilizing α-substituent have been less useful for the olefin synthesis because of the low efficiency of cycloelimination in comparison with their ligand-changed derivatives such as alkylphosphonic diamides,[2a] alkylphosphonothioates,[2b] alkyldiphenylphosphine oxides,[2c] and alkylphenylphosphinothioic amides.[2d] It is noteworthy in a view of their easy availabilities if the olefins could be synthesized from alkylphosphonates. We reported previously on the fluoride ion induced Horner-Emmons reactions of α-silylalkylphosphonates.[3] In this paper, we wish to report that β-hydroxyalkylphosphonates can afford the corresponding olefins only on treatment with a fluoride ion without use of any strong base.

The β-hydroxyalkylphosphonates (1a-e) were readily prepared by the reactions of dimethyl lithiomethylphosphonate with benzophenone, dibenzyl ketone, acetophenone, dodecanal, and cyclohexanone, respectively.[4]

$$(MeO)_2P(O)CH_2Li + RR'C{=}O \longrightarrow (MeO)_2P(O)CH_2CRR'OH \xrightarrow{F^-} (MeO)_2P(O)OH + CH_2{=}CRR'$$

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a: R=R'=Ph; b: R=R'=CH_2Ph; c: R=Me, R'=Ph; d: R=H, R'=$C_{11}H_{23}$; e: RR'=$(CH_2)_5$

A typical procedure of the olefin synthesis is as follows: a solution of dimethyl 2-hydroxy-2,2-diphenylethylphosphonate (1a)(0.545 g, 1.78 mmol) in N,N-dimethylformamide (DMF)(20 ml) was stirred at 55 °C for 16 h in the presence of CsF (1.03 g, 6.80 mmol) and its equimolar amount of water. After removal of the solvent, the residue was chromatographed on silica gel to give 1,1-diphenylethylene in 83% yield.

This method is applicable to various types of β-hydroxyalkylphosphonates [5] to afford the corresponding olefins in fairly good yields as shown in Table 1.

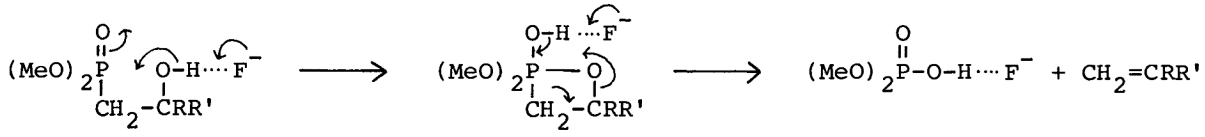
Table 1. THE OLEFIN SYNTHESIS FROM β-HYDROXYALKYLPHOSPHONATES (1a-e)[a]

$(MeO)_2P(O)CH_2CRR'OH$ 1	$CsF-H_2O$ equiv.[b]	Temp °C	Time h	$CH_2=CRR'$ Yield/%[c]
a: R=R'=Ph	3.8	55	16	83
	3.5	90	5	85
b: R=R'=CH_2Ph	2.8	90	48	85
c: R=Me, R'=Ph	2.6	80	9	76
d: R=H, R'=$C_{11}H_{23}$	3.5	90	48	62
e: RR'=$(CH_2)_5$	2.9	100	30	46

a) Solutions of 1a-e (0.30-7.40 mmol) in DMF (15-30 ml) were used.
b) Molar equivalent of $CsF-H_2O$ to 1.
c) Isolated yields based on 1.

Acetonitrile, 1,2-dimethoxyethane, and tetrahydrofuran can be used in place of DMF, but relatively drastic conditions were necessary. The reactions also proceed on using KF in refluxing DMF to give the comparable results, however, use of tetraalkylammonium fluorides resulted in poor yields of the olefins. The effect of additive water is considered probably to make the surface area of CsF increase through the formation of its hydrate as suggested in Knoevenagel reactions using $KF-2H_2O$.[6]

The reaction may proceed as shown in the following scheme, that is, an increase in hydrogen-bonding strength of a fluoride ion towards the hydroxyl group in the order of the reactant, the intermediate, and the product seems to be a driving force of the present reaction.[7]



The merits of the present method are easy availabilities of β-hydroxyalkylphosphonates and the applicability to synthesis of 1-alkenes [8] (see Table 1).

Further works are in progress.

References

1) B. J. Walker,"Organophosphorus Reagents in Organic Synthesis," ed by J. I. G. Cadogan, Academic Press, London-New York-Toronto-Sydney-San Francisco (1979), pp. 155-205.

2) See for examples: a) E. J. Corey and G. T. Kwiatkowski, J. Am. Chem. Soc., 88, 5652 (1966); b) E. J. Corey and G. T. Kwiatkowski, J. Am. Chem. Soc., 88, 5654 (1966); c) L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, Chem. Ber., 92, 2499 (1959); A. H. Davidson, I. Fleming, J. I. Grayson, A. Pearce, R. L. Snowden, and S. Warren, J. Chem. Soc., Perkin Trans. 1, 1977, 550; A. D. Buss and S. Warren, J. Chem. Soc., Chem. Commun., 1981, 100; d) C. R. Johnson and R. C. Elliott, J. Am. Chem. Soc., 104, 7041 (1982).

3) T. Kawashima, T. Ishii, and N. Inamoto, Tetrahedron Lett., 24, 739 (1983).

4) β-Hydroxyalkylphosphonates were prepared as described by Corey and Kwiatkowski.[2b] Dimethyl 2-hydroxy-2,2-diphenylethylphosphonate (1a): 96% yield; mp 102.0-103.0 °C (EtOH). Elementary analysis (EA): Found: C, 62.54; H, 6.29%. Calcd for $C_{16}H_{19}O_4P$: C, 62.74; H, 6.25%. ^{1}H-NMR ($CDCl_3$): δ 2.89 (d, $^2J_{PH}$= 17.6 Hz, 2H, PCH_2), 3.37 (d, $^3J_{PH}$= 11.0 Hz, 6H, $P(OCH_3)_2$), 5.59 (bs, 1H, OH), and 7.1-7.9 (m, 10H, $(C_6H_5)_2C$). ^{31}P-NMR ($CDCl_3$): δ_p 31.36 ppm (from 85%-H_3PO_4). Dimethyl 2,2-dibenzyl-2-hydroxyethylphosphonate (1b): 95% yield; mp 140.0-141.0 °C (EtOH:Hexane = 1:1). EA: Found: C, 64.69; H, 6.96%. Calcd for $C_{18}H_{23}O_4P$: C, 64.66; H, 6.93%. ^{1}H-NMR ($CDCl_3$): δ 1.93 (d, $^2J_{PH}$= 18.6 Hz, 2H, PCH_2), 2.92 (d, $^4J_{PH}$= 1.0 Hz, 4H, $(PhCH_2)_2C$), 3.58 (s, 1H, OH), 3.70 (d, $^3J_{PH}$= 11.0 Hz, 6H, $P(OCH_3)_2$), and 7.1-7.4 (m, 10H, $(C_6H_5CH_2)_2C$). ^{31}P-NMR ($CDCl_3$): δ_p 32.47 ppm. Dimethyl 2-hydroxy-2-phenylpropylphosphonate (1c): 96% yield; bp 120-125 °C/0.05 Torr. High resolu-

tion mass spectrum: m/e Found: 244.0842. Calcd for $C_{11}H_{17}O_4P$: 244.0862. ^{1}H-NMR ($CDCl_3$): δ 1.62 (d, $^4J_{PH}$= 2.2 Hz, 3H, C$\underline{H}_3$), 2.10-2.70 (m, 2H, PC$\underline{H}\underline{H}'$), 3.20 (d, $^3J_{PH}$= 11.0 Hz, 3H, P(OC$\underline{H}_3$)(OCH'$_3$)), 3.65 (d, $^3J_{PH}$= 11.0 Hz, 3H, P(OCH$_3$)(OC$\underline{H}'_3$)), 4.88 (bs, 1H, O$\underline{H}$), and 7.1-7.7 (m, 5H, $C_6\underline{H}_5$C). ^{31}P-NMR ($CDCl_3$): δ_p 31.28 ppm. Dimethyl 2-hydroxytridecylphosphonate (1d): 99% yield; mp 60.0-60.5 °C (Et_2O). EA: Found: C, 58.49; H, 10.71%. Calcd for $C_{15}H_{33}O_4P$: C, 58.42; H, 10.79%. ^{1}H-NMR ($CDCl_3$): δ 0.7-2.1 (m, 25H, $C_{11}\underline{H}_{23}$ + PC$\underline{H}_2$), 3.30 (bs, 1H, O$\underline{H}$), 3.76 (d, $^3J_{PH}$= 11.0 Hz, 3H, P(OC$\underline{H}_3$)(OCH'$_3$)), 3.77 (d, $^3J_{PH}$= 10.7 Hz, 3H, P(OCH$_3$)(OC$\underline{H}'_3$)), and 3.2-4.2 (m, 1H, C$\underline{H}$(OH)). ^{31}P-NMR ($CDCl_3$): δ_p 33.19 ppm. Dimethyl (1-hydroxycyclohexyl)methylphosphonate (1e): 83% yield; bp 135 °C/0.05 Torr. High resolution mass spectrum: m/e Found: 222.1047. Calcd for $C_9H_{19}O_4P$: 222.1022. ^{1}H-NMR ($CDCl_3$): δ 1.1-2.0 (m, 10H, $(C\underline{H}_2)_5$), 2.01 (d, $^2J_{PH}$= 18.1 Hz, 2H, PC$\underline{H}_2$), 3.67 (s, 1H, O$\underline{H}$), and 3.74 (d, $^3J_{PH}$= 11.0 Hz, 6H, P(OC$\underline{H}_3$)$_2$). ^{31}P-NMR ($CDCl_3$): δ_p 32.86 ppm.

5) β-Hydroxyalkylphosphonates obtained from alkylphosphonates other than dimethyl methylphosphonate can also afford the corresponding olefins. The results will be reported elsewhere.

6) F. Texier-Boullet and A. Foucaud, Tetrahedron Lett., 21, 2161 (1980); L. A. Carpino and A. C. Sau, J. Chem. Soc., Chem. Commun., 1979, 514.

7) J. H. Clark, Chem. Rev., 80, 429 (1980).

8) Johnson and Elliott [2d] reported that their method was not suitable for the synthesis of 1-alkenes such as 1-tridecene.

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