CHEMISTRY LETTERS, pp. 1097 - 1100, 1984. © The Chemical Society of Japan 1984

THE EFFECTIVENESS OF A WEAK BASE IN THE OLEFIN SYNTHESIS FROM β-HYDROXYALKYLPHOSPHONATES

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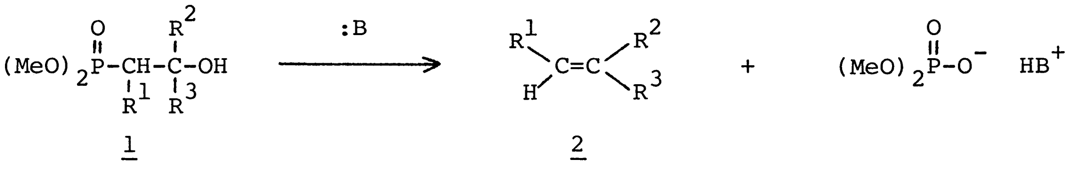
β-Hydroxyalkylphosphonates were treated with a weak base such as potassium carbonate in N,N-dimethylformamide to give the corresponding olefins in good yields.

During the course of an investigation on the Horner-Emmons reaction from the phosphoryl compounds without any carbanion stabilizing substituent at the α-position of the phosphorus atom,1) we previously reported on the fluoride ion induced olefin synthesis from β-hydroxyalkylphosphonates.2) It is useful to survey and to find out some effective reagents other than fluoride salts, because fluorides are sometimes expensive and their activities are very dependent on the used solvent and on an amount of water involved in the system.3)

We now wish to report that some weak bases can also convert the β-hydroxyalkylphosphonates (1), which can be readily prepared from the alkylphosphonates and the carbonyl compounds,4) into the corresponding olefins very efficiently.



a: R^1=H, R^2=R^3=CH_2Ph; b: R^1=H, R^2=Me, R^3=Ph; c: R^1=H, R^2R^3=$(CH_2)_5$;
d: R^1=R^2=H, R^3=$C_{11}H_{23}$; e: R^1=Me, R^2=R^3=Ph; f: R^1=Me, R^2=R^3=CH_2Ph

A typical procedure is described for the preparation of 1,1-dibenzylethylene (2a): Dimethyl 2,2-dibenzyl-2-hydroxyethylphosphonate (1a)(2.15 mmol) was treated for 48 h at 95 °C with potassium carbonate (15.6 mmol) and water (15.6 mmol) in N,N-dimethylformamide (DMF)(20 ml). The reaction mixture was diluted with water and extracted with pentane or ether. After the organic layer was washed with water several times and dried over anhydrous magnesium sulfate, removal of the solvent gave 1,1-dibenzylethylene (2a) in 78% yield in almost pure state.

This and other results are summarized in Tables 1 and 2.

Table 1. The synthesis of 1,1-dibenzylethylene (2a) from dimethyl 2,2-dibenzyl-2-hydroxyethylphosphonate (1a)[a)]

Run	1a mmol	Base[b)] mmol	Temp °C	Time h	Yield[c)] %
1	2.15	K_2CO_3-H_2O[d)] (15.6)	95	48	78
2	2.25	K_2CO_3-H_2O[d)] (12.1)	135	14	78
3	2.23	K_2CO_3-$2H_2O$ (13.4)	95-105	48	81
4	2.16	K_2CO_3 (12.8)	95	48	41 (21)[e)]
5	1.08	K_2CO_3-MeOH[d)] (4.99)	90-110	52	64
6	2.27	$KHCO_3$-H_2O[d)] (12.7)	135	14	66
7	1.13	Na_2CO_3-H_2O[d)] (6.64)	90	48	7.6 (76)[e)]
8	1.02	Cs_2CO_3-H_2O[d)] (6.1)	90	48	70
9	1.19	PhOLi (7.0)	85-100	0.5	77
10	2.18	PhONa (10.0)	100	1	66
11	1.12	PhOK (3.1)	90	1	72
12	1.05	DBU (5.0)	100-105	14	56
13	2.85	t-BuOK (7.1)	65	48	-[f)]
14	2.35	NaH (3.5)	rt	10	-[f)]
15	0.94	KH (1.41)	rt	10	-[f)]

a) All runs were carried out in DMF (10-20 ml). b) The molar ratio of the base to 1a is not optimized. c) Isolated yields based on 1a. d) Water or methanol was added in the equimolar amount to that of carbonate. e) Recovery of 1a was shown in parentheses. f) 1a was consumed, but no 2a was obtained.

Among alkali carbonates used, potassium or cesium carbonate gave a comparable result to each other, but sodium carbonate did not work well, probably because of the poor solubility. Dimethyl sulfoxide can be used as a solvent in place of DMF. An addition of water may increase the yield of the olefin as well as accelerate the reaction, presumably because of an increase of the surface area or the solubilities of the carbonates, however, alcohol is less effective than water. It is very interesting to point out that β-hydroxyalkylphosphonates can be converted into the corresponding olefins by action of a weak base such as potassium carbonate or DBU,$^{5)}$ which has been reported very recently to give no olefins from β-hydroxyalkyldiphenylphosphine oxides.$^{6)}$ Judging from the fact that the use of a stronger base such as sodium or potassium hydride and potassium t-butoxide causes only side reactions, an interaction such as hydrogen bonding of a weak base towards the hydroxyl group of 1 as described in the previous paper $^{2)}$ would play an important role in the present reaction rather than the generation of the completely free alkoxide.

The merits of this olefination are easy availability of β-hydroxyalkylphosphonates, which can be converted into the olefins without migration of the double bond only by treatment with a weak and cheap base and readiness of work-up (see typical procedure). Further investigations are in progress.

Table 2. The olefin synthesis from various β-hydroxyalkylphosphonates (1a-f) by treatment with an equimolar mixture of potassium carbonate and water

1 mmol	K_2CO_3-$H_2O$$^{a)}$ mmol	DMF ml	Temp °C	Time	2	Yield$^{b)}$ %
1a (2.15)	15.6	20	95	2 d	2a	78
1b (3.87)	21.1	35	85	40 h	2b	75
1c (8.63)	28.1	30	90-110	4 d	2c	52
1d (1.78)	10.0	20	90-110	4 d	2d	47
1e (1.44)	7.90	15	45-50	2 d	2e	91
1f (2.94)	20.0	30	90-110	2 d	2f	85

a) The molar ratio of the base to 1 is not optimized. b) Isolated yields based on 1a-f. The olefins were obtained in almost pure state even in the cases of low yields.

References

1) For recent examples see: A. D. Buss, N. Greeves, D. Levin, P. Wallace, and S. Warren, Tetrahedron Lett., 25, 357 (1984), and the references cited therein; A. D. Buss and S. Warren, J. Chem. Soc., Chem. Commun., 1981, 100; A. D. Buss and S. Warren, Tetrahedron Lett., 24, 111 (1983); C. R. Johnson, R. C. Elliott, and N. A. Meanwell, Tetrahedron Lett., 23, 5005 (1982); C. R. Johnson and R. C. Elliott, J. Am. Chem. Soc., 104, 7041 (1982).

2) T. Kawashima, T. Ishii, and N. Inamoto, Chem. Lett., 1983, 1375.

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

4) The β-hydroxyalkylphosphonates (1a-d) were prepared as described in Ref. 2. 1e and 1f were prepared by reactions of the α-lithio derivative of dimethyl ethylphosphonate with benzophenone and dibenzyl ketone, respectively. In the case of 1f, N,N,N',N'-tetramethylethylenediamine was used as a co-solvent. 1e: 96% yield; mp 113-114 °C (Et_2O); Elementary analysis (EA): Found: C, 63.47; H, 6.77%. Calcd for $C_{17}H_{21}O_4P$: C, 63.74; H, 6.61%. ^{1}H-NMR ($CDCl_3$): δ 1.24 (3H, dd, $^3J_{PH}$=17.6 Hz, $^3J_{HH}$=7.5 Hz, P-CH-C$\underline{H}_3$), 2.99 (3H, d, $^3J_{PH}$=10.8 Hz, P(OC$\underline{H}_3$)-(OCH'$_3$)), 3.59 (3H, d, $^3J_{PH}$=10.8 Hz, P(OCH$_3$)(OC$\underline{H}'_3$)), 3.0-3.8 (1H, m, P-C$\underline{H}$-), 5.31 (1H, br s, O$\underline{H}$), and 7.1-7.7 (10H, m, C(C$_6\underline{H}_5$)$_2$); ^{31}P-NMR ($CDCl_3$): δ_P 35.72 ppm (from external H_3PO_4); MS (70 eV): m/e 320 (M^+, 2.5%) and 138 (M^+-Ph_2CO, 100). 1f: 80% yield; mp 94.7-95.5 °C (Et_2O); EA: Found: C, 65.35; H, 6.95%. Calcd for $C_{19}H_{25}O_4P$: C, 65.51; H, 7.23%. ^{1}H-NMR ($CDCl_3$): δ 1.23 (3H, dd, $^3J_{PH}$=17.7 Hz, $^3J_{HH}$=7.4 Hz, P-CH-C$\underline{H}_3$), 1.8-2.3 (1H, m, p-C$\underline{H}$-), 2.6-3.3 (4H, m, C(C$\underline{HH}$'-Ph)$_2$), 3.62 (3H, d, $^3J_{PH}$=10.5 Hz, P(OC$\underline{H}_3$)(OCH'$_3$)), 3.77 (3H, d, $^3J_{PH}$=10.5 Hz, P(OCH$_3$)(OC$\underline{H}'_3$)), 4.39 (1H, br s, O$\underline{H}$), and 7.2-7.9 (10H, m, C(CHH'-C$_6\underline{H}_5$)$_2$); ^{31}P-NMR ($CDCl_3$): δ_P 36.14 ppm; MS: m/e 348 (M^+, 0.55%) and 91 ($PhCH_2^+$, 100).

5) A weaker base such as pyridine, sodium acetate, potassium oxalate or basic alumina than the bases used here is ineffective.

6) A. D. Buss, W. B. Cruse, O. Kennard, and S. Warren, J. Chem. Soc., Perkin Trans. 1, 1984, 243.

(Received April 14, 1984)