Tetrahedron Letters,Vol.24,No.7,pp 739-742,1983 0040-4039/83/070739-04$03.00/0
Printed in Great Britain

FLUORIDE ION INDUCED HORNER-EMMONS REACTION OF α-SILYLALKYLPHOSPHONATES WITH CARBONYL COMPOUNDS

Takayuki KAWASHIMA, Takafumi ISHII, and Naoki INAMOTO*
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract: α-Trimethylsilylalkylphosphonates react with carbonyl compounds to give the corresponding olefins in the presence of fluoride ion. Use of CsF gave the best result.

Since Si-F bond energy is high,[1] fluoride ion induced desilylation has been utilized as a powerful tool for the generation of stabilized carbanions under neutral and relatively mild conditions.[2] The first application to the Wittig reaction was demonstrated by Vedejs [3] and desilylation of α-silylalkylphosphonium salts has been shown to be a useful synthetic method for tri-substituted olefins, very recently.[4]

Here we wish to report the Si-C bond of α-silylalkylphosphonates [5] can also be cleaved by action of fluoride ion to generate reactive species for the Horner-Emmons reaction.

Dimethyl α-trimethylsilylbenzylphosphonate (1a)[6] (2 mmol) was reacted in THF (20 ml) with benzaldehyde (4 mmol) in the presence of various fluoride ions (3 m-mol) to give stilbene and dimethyl benzylphosphonate (2a). The results were summarized in Table 1. The monitoring by ^{31}P-NMR indicated that as the peak due to 1a decreased gradually, the signal of protodesilylation product (2a) appeared, but no peak of the phosphate ion could be observed except for use of tetrabutylammonium fluoride (TBAF) because of the low solubility. A similar result was obtained in acetonitrile, but in toluene the reaction was very slow. The reaction likely proceeds as shown in the following scheme.

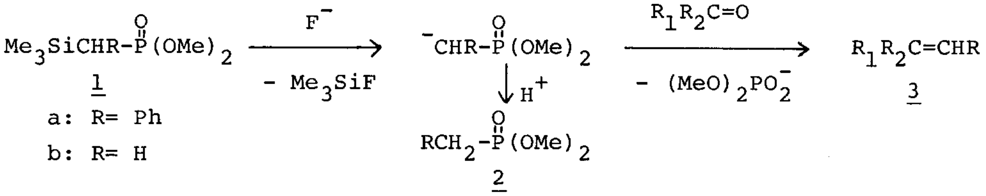


Table 1. Reaction of 1a with benzaldehyde in the presence of various fluoride ions in THF

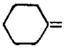
Fluoride[a)]	Reaction Conditions		Stilbene	
	Temp.	Time	Yield (%)[b)]	E/Z[c)]
CsF	reflux	5-6 h	85	100/0
KF-18-crown-6	reflux	2 days	20	100/0
TBAF	rt	30 min	60	90/10
Me_4NF	rt	1.5 h	30	90/10

a) Fluoride compounds were dried over P_2O_5 under vacuum with heating;
b) Isolated yields based on 1a; c) By ^1H-NMR analysis.

Ammonium fluorides can cause desilylation efficiently at room temperature, but yields of stilbene were rather poor, probably because of the difficulty in drying due to the thermal instability [2d] and the presence of acidic hydrogens easily abstractable by the resulting carbanion. Therefore, CsF seems to the most suitable for the present reaction, and was used in the reactions with other carbonyl compounds (Table 2).

It is noteworthy that α-methylstilbene was obtained from acetophenone in a moderate yield, whereas the yield was less than 5% in the reaction using lithio derivative which deprotonated acetophenone mainly, suggesting that the carbanion generated by the present desilylation is less basic than the lithio derivative.

Table 2. CsF-induced reactions of 1a with carbonyl compounds in refluxing THF overnight[a)]

Carbonyl Compound	Olefin	Yield (%)[b)]
$Ph_2C=O$	$Ph_2C=CHPh$	79
PhMeC=O	PhMeC=CHPh (E/Z; 25/75)[c)]	67
=O	=CHPh	35
(E)-PhCH=CHCHO	PhCH=CHCH=CHPh (E,E)[d)]	65
i-PrCHO	i-PrCH=CHPh (E/Z; 70/30)[e)]	30

a) A mixture of 1a (2 mmol), carbonyl compound (4-6 mmol), CsF (3 mmol), and THF (20 ml) was used.

b) Isolated yields based on 1a.

c) E/Z ratio was determined by ^{1}H-NMR analysis; A. F. Casey et al., Tetrahedron, 24, 3031 (1968).

d) J. H. Pinckard et al., J. Am. Chem. Soc., 70, 1938 (1948).

e) The lower field one of signals due to isopropyl groups was assigned to E-isomer.

On the other hand, the reaction of dimethyl α-trimethylsilylmethylphosphonate (1b) with benzophenone afforded dimethyl 2,2-diphenylethenylphosphonate (30%) besides 1,1-diphenylethylene (20%) and 2b (50%). From the facts that the carbanion with both silyl and phosphoryl groups at α-position reacts with carbonyl compounds to give vinylphosphonates by selective elimination of siloxide anion [7] and that dimethyl 2,2-diphenyl-2-trimethylsiloxyethylphosphonate (4)[8] afforded 1,1-diphenylethylene with CsF almost quantitatively,[9] it is reasonably concluded that the resulting phosphonate carbanion may competitively abstract proton from 1b to give α-silylphosphonate carbanion which causes the confused reaction.

Further works are in progress.

References and Notes

1. L. H. Sommer," Stereochemistry, Mechanism, and Silicon," McGraw Hill, New York, 1965, 25 pp.
2. Silyl enol ethers: (a) I. Kuwajima and E. Nakamura, J. Am. Chem. Soc., 97, 3259 (1975); (b) W. A. Kleschick, C. T. Buse, and C. H. Heathcock, ibid., 99, 247 (1977); (c) R. Noyori, K. Yokoyama, J. Sakata, I. Kuwajima, E. Nakamura, and M. Shimizu, ibid., 99, 1265 (1977); (d) I. Kuwajima and E. Nakamura, and M. Shimizu, ibid., 104, 1025 (1982); Allylsilanes: (e) A. Hosomi, A. Shirahata, and H. Sakurai, Tetrahedron Lett., 1978, 3043; Propargylsilanes: (f) J. Pornet, ibid., 22, 455 (1981); 2-Silyl-1,3-dithianes: (g) N. H. Andersen, D. A. McCrae, D. B. Grotjahn, S. Y. Gabhe, L. J. Theodore, R. M. Ippolito, and T. K. Sarkar, Tetrahedron, 37, 4069 (1981).
3. E. Vedejs and G. R. Martinez, J. Am. Chem. Soc., 101, 6452 (1979); Desilylation by chloride ion occurrs at elevated temperature but treatment with KF-18-crown-6 or TBAF results in protodesilylation: A. Sekiguchi and W. Ando, J. Org. Chem., 44, 413 (1979).
4. H. J. Bestmann and A. Bomhard, Angew. Chem. Int. Ed. Engl., 21, 545 (1982).
5. α-Silylalkylphosphonates are known to rearrange at 250°C to give alkylidenesiloxyphosphoranes via 1,3-silyl migration which can undergo in situ Wittig reaction: A. Sekiguchi and W. Ando, Chem. Lett., 1978, 1385.
6. 1a was prepared in 92% yield by lithiation and silylation of 2a; bp 90-92°C/0.05 Torr; ^{1}H-NMR ($CDCl_3$): δ 0.13 (s, 9H), 2.73 (d, $J_{P,H}^2$ =25Hz, 1H), 3.56 (d, $J_{P,H}^3$ =11Hz, 3H), 3.68 (d, $J_{P,H}^3$ =11Hz, 3H), and 7.1-7.4 (m, 5H); ^{31}P-NMR ($CDCl_3$): δ_p 31.4 ppm (from 85%-H_3PO_4); Mass spectrum: m/e 272 (M^+, 49%), 257 (43), 167 (33), 151 (96), and 105 (100); Elementary analysis: Found: C, 53.04; H, 7.80%. Calcd for $C_{12}H_{21}O_3PSi$: C, 52.92; H, 7.77%.
7. F. A. Carey and A. S. Court, J. Org. Chem., 37, 939 (1972).
8. 4 was prepared in 95% yield by consequent reactions of 1b with BuLi, benzophenone (at -78°C), and chlorotrimethylsilane (at room temperature); mp 86-88°C (hexane); ^{1}H-NMR ($CDCl_3$): δ -0.04 (s, 9H), 3.05 (d, $J_{P,H}^2$ =19.6Hz, 2H), 3.42 (d, $J_{P,H}^3$ =11.0Hz, 6H), and 7.1-7.3 (m, 10H); ^{31}P-NMR ($CDCl_3$): δ_p 29.0 ppm; Mass spectrum: m/e 378 (M^+, 2.0%), 363 (59), 301 (33), and 255 (100); Elementary analysis: Found: C, 60.02; H, 7.07%. Calcd for $C_{19}H_{27}O_4PSi$: C, 60.30; H, 7.19%.
9. Cesium cation as counter cation seems to be very effective for the formation of β-hydroxyalkylphosphonate: cf. Use of potassium cation gave olefin in 30% yield; E. J. Corey and G. T. Kwiatkowski, J. Am. Chem. Soc., 88, 5654 (1966).

(Received in Japan 8 November 1982)