Tetrahedron Letters, Vol.31, No.20, pp 2901-2904, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

ALLYLIC 1,3-REARRANGEMENT OF 1-ALKOXYALLYLPHOSPHONIUM SALTS. REGIOCHEMISTRY OF REACTION OF 1-ALKOXY-2-ALKENYLENEPHOSPHORANES WITH ALDEHYDES

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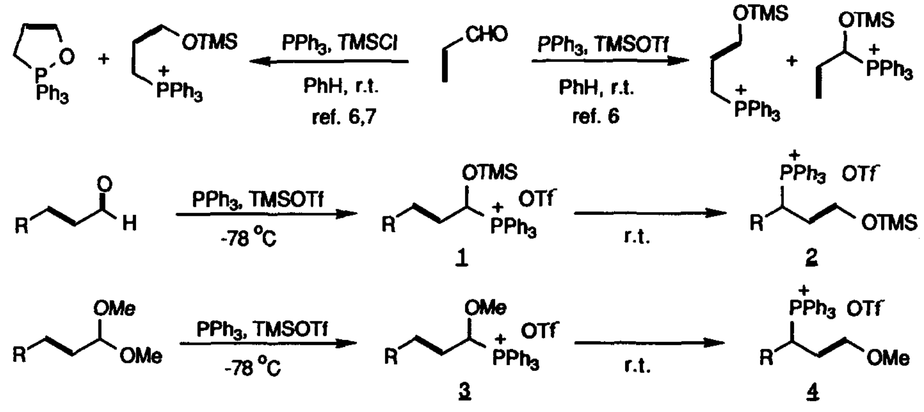
Summary: It was found that 1-alkoxyallylphosphonium salts underwent allylic 1,3-rearrangement to afford 3-alkoxyallylphosphonium salts. Reaction of 1-alkoxy-2-alkenylenephosphoranes with aldehydes gave α-adducts, whereas the reaction in the presence of TMSOTf gave γ-adducts.

It has been well recognized that α-heteroatom substituted allylic anions are useful precusors for reversed polarity equivalents in the carbon-carbon bond formation, but also that there is a problem with regioselectivity of reaction with electrophiles.[1] α-Alkoxyallylic phosphorous ylides with high γ-regioselectivity have been known to serve as homoenolate anions.[2-4] We wish to report (i) allylic 1,3-rearrangement of 1-alkoxyallylphosphonium salts[5] and (ii) complete regiocontrol in the reaction of 1-alkoxy-2-alkenylenephosphoranes with aldehydes.

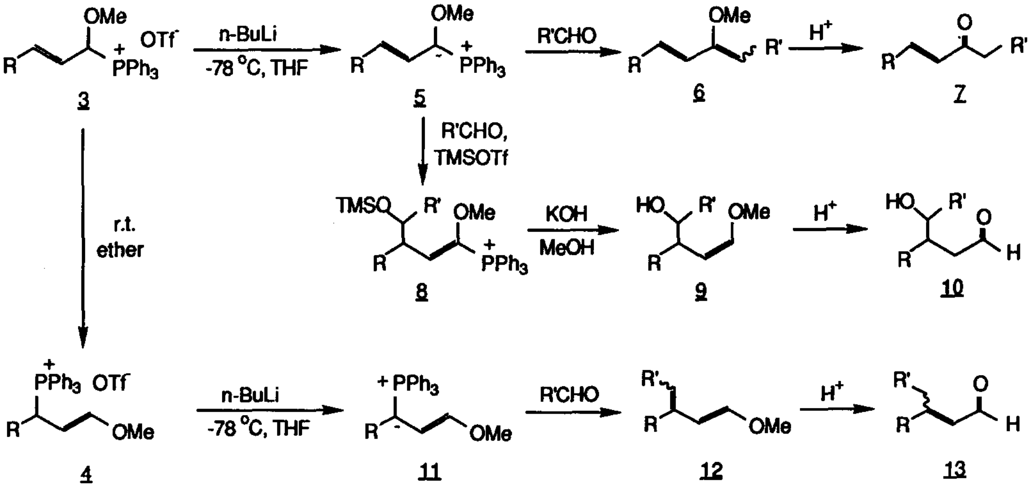
Previous studies on phosphoniosilylation of acrolein are shown in Scheme 1,[6,7] indicating 1,4-addition product as a major product along with 1,2-addition product. In contrast to these results, it was found that phosphoniosilylation of 2-enals with triphenylphosphine and trimethylsilyl triflate (TMSOTf) at -78 °C yielded the kinetically formed 1-silyloxyallylphosphonium salts (1) which were cleanly rearranged to thermodynamically favored 3-silyloxyallylphosphonium salts (2) upon warming to room temperature.[7] Similar results were obtained with α,β-unsaturated acetals. The formation of 1 and 3 and the subsequent allylic 1,3-rearrangement could be monitored by low temperature ^{1}H-NMR.[8,9]



Scheme 1

Allylic rearrangement of 1 in deuterochloroform was complete within 3 h at room temperature, whereas that of 3 required 5 h. Allylic 1,3-rearrangement can be performed on etheral and halogenated solvents. However, tetrahydrofuran is not suitable because TMSOTf leads to polymerization of tetrahydrofuran to some extent at room temperature.

Regiochemical control in reactions of 1-alkoxy-2-alkenylenephosphoranes (5) with aldehydes was studied.[10] In contrast to predominant γ-regioselectivity obtained with α-alkoxyallyl phosphorous related ylides,[2-4] reaction of the ylide (5, R=Me) with benzaldehyde in tetrahydrofuran at -78 °C followed by warming to 0 °C over 30 min afforded 1-phenyl-2-methoxy-1,3-pentadiene in 90% yield, which was further subjected to acidic hydrolysis to give 1-phenyl-3-penten-2-one.[11] As shown in Table 1, similar results were obtained with several 5 and α-regioselectivity was not affected with the structural change of aldehydes and 5.

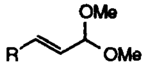
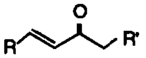
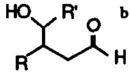
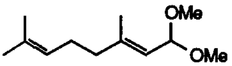
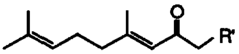
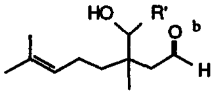
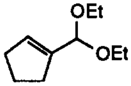
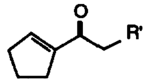
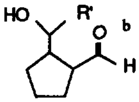


Scheme 2

The dramatic change in regiochemistry was realized when the reaction was carried out in the presence of TMSOTf.[12] Thus, the reaction of 5 (R=Me) with equimolar amounts of benzaldehyde and TMSOTf in tetrahydrofuran at -78 °C afforded exclusively γ-hydroxyalkylated vinylphosphonium salt (8) which was further subjected to methanolic potassium hydroxide at room temperature for 1 h to give exclusively Z-methyl enol ether (9). Subsequent acidic hydrolysis of 9 gave the γ-hydroxyalkylated aldehyde (10) in 77% yield. As shown in Table 1, similar results were obtained with structurally different aldehydes. Thus, 1-alkoxy-2-alkenylenephosphoranes can be regarded as both α,β-unsaturated acyl and homoenolate anion equivalents.[1]

Allylic 1,3-rearrangement of 3 to 4 in ether at room temperature for 5 h, treatment with n-butyllithium, and reaction with aldehydes gave 1-methoxy-1,3-dienes (12) which

Table 1. Reaction of 1-Alkoxy-2-alkenylenephosphoranes with Aldehydes

acetal	aldehyde	product	yield, %[a]
			
R=CH_3	C_6H_5CHO	R'=C_6H_5	81
R=n-C_6H_{13}	C_6H_5CHO	C_6H_5	84
	n-$C_8H_{17}CHO$	n-C_8H_{17}	71
	c-$C_6H_{11}CHO$	c-C_6H_{11}	68
		 [b]	
R=CH_3	C_6H_5CHO/TMSOTf	R'=C_6H_5	77
R=n-C_6H_{13}	C_6H_5CHO/TMSOTf	C_6H_5	78
	n-$C_8H_{17}CHO$/TMSOTf	n-C_8H_{17}	75
	c-$C_6H_{11}CHO$/TMSOTf	c-C_6H_{11}	76
			
	C_6H_5CHO	R'=C_6H_5	85
	n-$C_8H_{17}CHO$	n-C_8H_{17}	73
		 [b]	
	C_6H_5CHO/TMSOTf	R'=C_6H_5	74
	n-$C_8H_{17}CHO$/TMSOTf	n-C_8H_{17}	75
			
	C_6H_5CHO	R'=C_6H_5	62
	n-$C_8H_{17}CHO$	n-C_8H_{17}	59
		 [b]	
	C_6H_5CHO/TMSOTf	R'=C_6H_5	53
	n-$C_8H_{17}CHO$/TMSOTf	n-C_8H_{17}	51

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[a] The yields refer to isolated products based on α,β–unsaturated acetals.

[b] The presence of syn- and anti-isomers roughly in the equal ratio was indicated by ^{1}H-NMR analysis.

were subjected to acidic hydrolysis to give β-alkylated enals (13) in good yields.[13] The results obtained in this study were in accordance with the previous reports.[14] However, in contrast to the results obtained with 5, the regiochemistry of the reaction in the presence of TMSOTf was not affected, yielding only TMS quenched betaine intermediate. This phenomenon may be attributed to the anion destabilizing effect at α position by oxygen atom.[15]

References and Notes

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5. For recent examples of allylic 1,3-rearrangement, see: K. Ogura, T. Iihama, S. Kiuchi, T. Kajiki, O. Koshikawa, K. Takahashi and H. Iida, *J. Org. Chem.*, **50**, 700 (1986); A. Padwa, W. H. Bullock and A. D. Dyszlewski, *Tetrahedron Lett.*, **28**, 3193 (1987); J. A. Marshall and W. Y. Gung, *Ibid.*, **30**, 2183 (1989).
6. A. P. Kozikowski and S. H. Jung, *J. Org. Chem.*, **51**, 3402 (1986).
7. 1-Silyloxyallylphosphonate is known to be stable up to 200 °C. D. A. Evans, K. M. Hurst and J. M. Takacs, *J. Am. Chem. Soc.*, **100**, 3467 (1978).
8. Pure E-isomers of 2 and 4 were obtained according to ^{1}H-NMR analysis.
9. 1(R=Me) ^{1}H-NMR ($CDCl_3$, -50 °C) δ 0.12 (s, 9H), 1.77-1.80 (t, 3H, J=5.4 Hz) 5.55-5.64 (m, 1H), 6.08-6.17(m, 1H), 6.21-6.25(m, 1H), 7.73-7.91(m, 15H); 2 (R=Me) ^{1}H-NMR($CDCl_3$, 20 °C) δ 0.10(s, 9H), 1.38(dd, 3H, J=6.9, 18.6 Hz), 4.49-4.58 (ddd, 1H, J=5.5, 10.0, 11.7 Hz), 4.97-5.07(m, 1H), 6.80(dd, 1H, J=5.0, 11.7 Hz), 7.66-7.85(m, 15H); 3 (R=Me) ^{1}H-NMR ($CDCl_3$, -50 °C) δ 1.66-1.70(t, 3H, J=5.1 Hz), 3.44(s, 3H), 5.26-5.36(m, 1H), 5.78(t, 1H, J=7.6 Hz), 6.03-6.12(m, 1H), 7.61-7.79(m, 15H); 4 (R=Me) ^{1}H-NMR ($CDCl_3$, 20 °C) δ 1.39(dd, 3H, J=6.9, 18.1 Hz), 3.32(s, 3H), 4.17-4.26(ddd, 1H, J=5.3, 9.6, 12.5 Hz), 4.86-4.95(m, 1H), 6.67(dd, 1H, J=4.8, 12.5 Hz), 7.58-7.77(m, 15H).
10. Similar reactions with 1-silyloxyallylphosphonium salt failed to give the desired product due in part to the instability of the ylide.
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13. 13(R=n-C_6H_{13}, R'=Ph): 74%; 13(R=n-C_6H_{13}, R'=n-C_8H_{17}): 61%.
14. S. F. Martin and P. J. Garrison, *Tetrahedron Lett.*, **18**, 3875 (1977); A. P. Kozikowski and S. H. Jung, *Ibid.*, **27**, 3227 (1986).
15. This research was financially supported by Korea Science and Engineering Foundation.

(Received in Japan 19 January 1990)