Pergamon

Tetrahedron Letters, Vol. 36, No. 27, pp. 4833-4836, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(95)00905-1

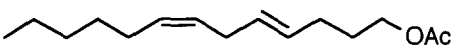
Nonconjugated Dienes from 1-Alkenes: Application to the Synthesis of Sex Pheromone (4*E*,7*Z*)-4,7-Tridecadienyl Acetate

Taek Hyeon Kim* and Ki Man Park

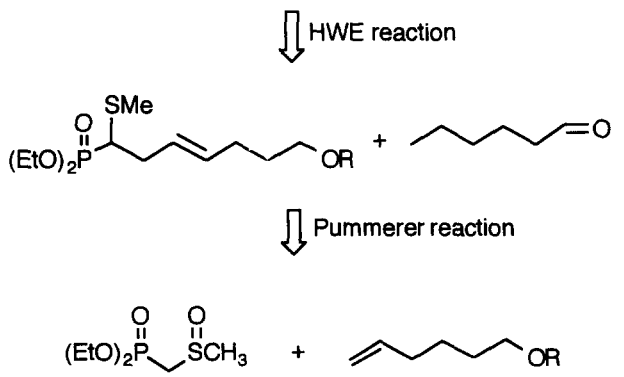
Department of Fine Chemical Technology, Chonnam National University, Kwangju 500-757, Korea

Abstract: (4*E*,7*Z*)-4,7-Tridecadienyl acetate **1**, a component of the sex pheromone was synthesized from 5-hexenyl acetate. (*E*)-γ,δ-Unsaturated phosphonate as the key intermediate afforded a target molecule, using the Horner-Wadsworth-Emmons (HWE) reaction and desulfonylation as the main process.

Diene systems are widely encountered in sex pheromones.[1] (4*E*,7*Z*)-4,7-Tridecadienyl acetate **1**, a component of the sex pheromone of the potato tuberworm moth (*Phthorimaea operculella*),[2] is prepared mainly from the stereoselective transformation of appropriate acetylene,[2, 3] Claisen rearrangement reaction,[4] and a specific method.[5]



1, (4E, 7Z)-4, 7-Tridecadienyl acetate

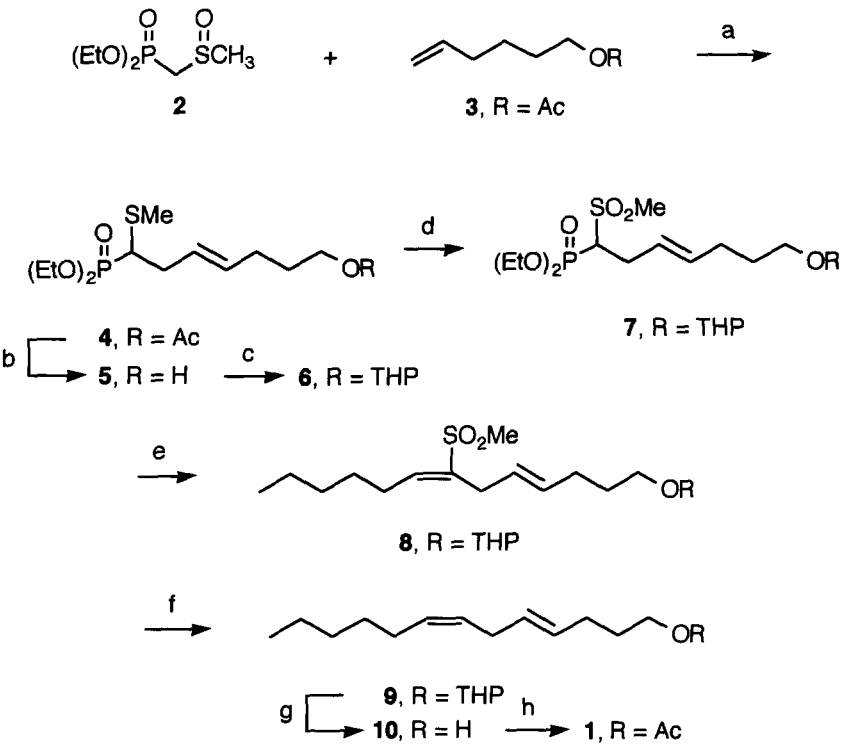


Scheme I

In our continuing studies on the α-heteroatom substituted phosphonates,[6] we found the Pummerer reaction of methylsulfinyl methanephosphonate with 1-alkenes stereoselectively gave the (*E*)-γ,δ-unsaturated phosphonate.[7,8] Phosphonates are an important reagent for the construction of carbon-carbon double bonds, because their use provides control of olefin regio-and stereoselectivity.[9] We projected that such a γ,δ-unsaturated

phosphonate analogue would be a significant precursor for the synthesis of **1**, using the Horner-Wadsworth-Emmons (HWE) reaction for the stereochemical control of C7 position (**Scheme I**).

We used a protected 5-hexen-1-ol as the starting material to investigate the route outlined in Scheme I. Pummerer rearrangement of methylsulfinyl methanephosphonate **2** with 5-hexenyl acetate **3** with trifluoroacetic anhydride (TFAA) in trifluoroacetic acid (TFA) afforded 7-acetoxy-1-methylthiohept-3-enyl phosphonate **4** in 83% yields. The *E* and *Z* ratio of **4** was determined to be 85:15 by capillary GC and also by ^{1}H-NMR after the next HWE reaction. Deprotection of **4** with K_2CO_3/ MeOH-H_2O followed by reprotection of hydroxy group **5** with 3, 4-dihydro-2*H*-pyran led to THP ether **6** in high overall yields. The HWE reaction of **6** with hexanal failed to generate the carbon-carbon double bond.



Scheme II *Reagents and conditions*: (a) TFAA, TFA, rt (82%);(b) K_2CO_3, MeOH, H_2O, rt (85%);(c) 3,4-dihydro-2H-pyran, PPTS, CH_2Cl_2, rt (95%); (d) *m*-CPBA, $CHCl_3$, 0 °C-rt (80%); (e) n-BuLi, THF, -78 °C-rt (86%); (f) sodium hydrosulfite, $NaHCO_3$, EtOH, H_2O, 80 °C (42%); (g) PPTS, MeOH, 50 °C (67%); (h) Ac_2O, DMAP, Pyridine.[2-5]

We turned to a more reactive sulfonyl group which would be removed readily. Methylsulfonyl phosphonate **7** was readily prepared by oxidation of THP ether with a excess *m*-chloroperbenzoic acid (*m*-CPBA), whereas using an excess sodium metaperiodate gave sulfoxide. The HWE reaction of lithium carbanion of **7** with hexanal successfully led to the required 1,4-diene system **8** in 86 % yields. The configuration of *E* and *Z* isomers of the vinyl sulfone **8** was determined with a ratio *E*:*Z*=70:30 on the basis of ^{1}H-NMR and could be separated by column chromatography on silica gel using mixed solvent, hexane:ethyl acetate=7:3. It should be

noted that the configuration of isomers **8** leading to a desired sex pheromone after the stereospecific desulfonylation is (4*E*,7*E*)-7-methylsulfonyl-1-(tetrahydro-2*H*-pyran-2-yl)oxy-4, 7-tridecadiene.

The methods of desulfonylation of vinyl sulfones have been found in a number of literature, in some cases stereospecifically.[10] Desulfonylation of the mixed isomers **8** with sodium hydrosulfite led to **9**, which was deprotected using pyridinium *p*-toluene sulfonate (PPTS) to provide the well-known alcohol **10**. The synthetic **10** has identical spectroscopic data with that of reported compound.[3-5] The synthesis of target acetate **1** from **10** is well-known process.[2-5] The structures of all the compounds were confirmed by spectral methods, NMR, IR, and Mass spectrocopy and comparison with the known products.[11]

This synthetic strategy successfully led to a target sex pheromone. Furthermore, considering the nature of the transformation, one would expect such a process for preparing a nonconjugated diene system from 1-alkene to be quite general.

Acknowledgements: Financial support for this work (1992) from Chonnam National University Research Foundation is gratefully acknowledged. Appreciation is expressed to OPC Laboratory in Korea Advanced Institute of Science and Technology for providing mass spectrum.

REFERENCES AND NOTES

1. Henrick, C. A. *Tetrahedron* **1977**, *33*, 1845-1889.
2. Roelofs, W. L.; Kochansky, J. P.; Carde, R. T.; Henrick, C. A.; Labovitz, J. N.; Corbin, V. L. *Life Sci.* **1975**, *17*, 699-706.
3. (a) Bestmann, H. J.; Zeibig, T.; Vostrowsky, O. *Synthesis.* **1990**, 1039-1047. (b) Yadav, J. S.; Reddy, P. S. *Synth. Commun.* **1986**, *16*, 1119-1131. (c) Nishiyama, H.; Sakuta, K.; Itoh, K. *Tetrahedron Lett.* **1984**, *25*, 223-226.(d) Fujisawa, T.; Sato, T.; Kawashima, M.; Naruse, K.; Tamai, K. *Ibid.* **1982**, *23*, 3583-3586. (e) Alexakis, A.; Cahiez, G.; Normant, J. F. *Ibid.* **1978**, 2027-2010. (f) Voerman, S.; Rothvhild, J. *J.Chem. Ecol.* **1978**, *4*, 531-542.
4. (a) Nonoshita, K.; Banno, H.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 316-322. (b) Chattopadhyay, A.; Mamdapur, V. R.; Chadha, M. S. *Indian J. Chem., Sect. B* **1987**, *26B*, 187-188. (c) Yadav, J. S.; Kulkarni, A. D.; Reddy, P. S. *Ibid.* **1986**, *25B*, 1220-1223. (d) Vig, O. P.; Sharma, M. L.; Kumari, S.; Rani, V. *Ibid.* **1985**, *24B*, 675-676.
5. Moiseenkov, A. M.; Cheskis, B. A.; Ivanova, N. M.; Nefedov, O. M. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2639-2649.
6. (a) Kim, T. H.; Oh, D. Y. *Synth. Commun.* **1994**, *24*, 2313-2318. (b) Kim, T. H.; Park, B. H.; Oh, D. Y. *Bull. Korean Chem. Soc.* **1994**, *15*, 1004-1005. (c) Lee, J. W.; Kim, T. H.; Oh, D. Y. *Synth. Commun.* **1989**, *19*, 2633-2637. (d) Oh, D. Y.; Kim, T. H.; Kang, D. H. *Bull. Korean Chem. Soc.* **1987**, *8*, 219. (e) Kim, T. H.; Oh, D. Y. *Tetrahedron Lett.* **1986**, *27*, 1165-1166. (f) Kim, T. H.; Oh, D. Y. *Ibid*, **1985**, *26*, 3479-3482.
7. Our unpublished data.
8. Ishibashi, H.; Sato, T.; Irie, M.; Ito, M.; Ikeda, M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1095-1098.
9. (a) Kelly, S. E. In *Comprehensive Organic Synthesis, Additions to C-X π Bonds, Part 1*; Schreiber, S. L., Ed.; Pergamone Press: Oxford, 1991; Vol 1; Chapter 3.1; pp. 755-781. (b) Maryanoff, B. E.; Reitz,

A. B. *Chem. Rev.* **1989**, *89*, 863-927. (c) Gosney, I.; Rowley, A. G. In *Organophosphorus Reagents in Organic Synthesis*; Cadogan, J. I. G., Ed.; Academic Press: New York, 1979; Chapter 2; pp. 17-153. (d) Walker, B. J. In *Organophosphorus Reagents in Organic Synthesis*; Cadogan, J. I. G., Ed.; Academic Press: New York, 1979; Chapter 3; pp. 155-205. (e) Wadsworth, W. S. Jr.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1733-1738. (f) Horner, L.; Hoffmann, H.; Wippel, H. G. *Chem Ber.* **1958**, *91*, 61-63.

10. Back, T. G.; Collins, S.; Krishna, M. V.; Law, K. W. *J. Org. Chem.* **1987**, *52*, 4258-4264. and references cited therein.

11. Compound **4**. ^{1}H NMR($CDCl_3$) δ 1.32-1.38(t, 6H), 1.71(quintet, 2H, J=7.0 Hz), 2.04(s, 3H), 2.24(s, 3H), 2.24-2.20(m, 2H), 2.30-2.73(m, 3H), 4.05(t, 2H, J=7.0 Hz), 4.13(dq, 4H, J=7.7 Hz), 5.53-5.58(m, 2H); IR 1740(s), 1244(vs), 1028(vs); Mass: m/e(%) 81(25.0), 93(39.4), 125(38.0), 141(44.2), 198(100.0), 338(M^+, 3.2).

Compound **5**. ^{1}H NMR($CDCl_3$) δ 1.27(t, 6H, J=7.0 Hz), 1.57(quintet, 2H, J=7.0 Hz), 2.03-2.14(m, 2H), 2.16(s, 3H, *E isomer*), 2.17(*Z isomer*), 2.20-2.64(m, 3H), 3.55(t, 2H, J=6.5 Hz), 4.12(dq, 4H, J=7.7 Hz), 5.44-5.54(m, 2H); IR 3424(m), 1232(s), 1028(vs); Mass: m/e(%) 125(21.8), 141(21.9), 152(32.0), 198(100.0), 296(0.8, M^+).

Compound **6**. ^{1}H NMR($CDCl_3$) δ 1.34(t, 6H, J=7.0 Hz), 1.53-1.85(m, 8H), 2.12-2.16(m, 2H), 2.23(s, 3H), 2.25-2.70(m, 3H), 3.32-3.52(m, 2H), 3.68-3.88(m, 2H), 4.18(dq, 4H, J=7.7 Hz), 4.57(bs, 1H), 5.49-5.63(m, 2H); IR 1244(s), 1030(vs); Mass: m/e(%) 93(15.0), 152(18.5), 198(100.0).

Compound **7**. ^{1}H NMR($CDCl_3$) δ 1.33-1.39(t, 6H), 1.42-1.89(m, 8H), 2.03-2.18(m, 2H), 2.18-3.00(m, 3H), 3.20(s, 3H), 3.30-3.68(m, 2H), 3.68-3.90(m, 2H), 4.15(dq, 4H, J=7.7 Hz), 4.57(bs, 1H), 5.48-5.72(m, 2H); IR 1311(s), 1250(s), 1022(vs); Mass: m/e(%) 55(46.3), 84(52.9), 93(64.3), 175(50.4), 203(100.0), 230(57.6).

Compound **8**. ^{1}H NMR($CDCl_3$) *7-E isomer* δ 0.89(t, 3H), 1.25-1.33(m, 4H), 1.50-1.88(m, 10H), 2.03-2.10(m, 2H), 2.10-2.22(m, 2H), 2.84(s, 3H), 3.20(bd, 2H), 3.35-3.50(m, 2H), 3.68-3.85(m, 2H), 4.55(s, 1H), 5.39-5.49(m, 1H), 5.50-5.59(m, 1H), 6.81(t, 1H); *7-Z isomer* 0.89(t, 3H), 1.25-1.89(m, 14H), 2.08-2.19(m, 2H), 2.51-2.63(m, 2H), 2.90(s, 3H), 3.10(bd, 2H), 3.35-3.50(m, 2H), 3.68-3.85(m, 2H), 4.57(bd, 1H), 5.39-5.49(m, 1H), 5.50-5.59(m, 1H), 6.09(t, 1H); IR 2932-2862(s), 1304(s), 1126(s); Mass: m/e(%) 55(42.0), 67(33.8), 85(100.0), 120(35.9).

Compound **9**.[5] ^{1}H NMR($CDCl_3$) δ 0.89(t, 3H, J=6.8 Hz), 0.95-1.72(m, 14H), 1.80-2.17(m, 4H), 2.44-2.82(m, 2H), 3.32-3.42(m, 2H), 4.28-4.56(m, 2H), 4.66(s, 1H), 5.14-5.48(m, 4H).

Compound **10**.[3-5] ^{1}H NMR($CDCl_3$) δ 0.90(t, 3H), 1.15-1.34(m, 8H), 1.80-2.17(m, 4H), 2.56-2.78(m, 2H), 3.60(t, 2H, J=6.0 Hz), 5.25-5.85(m, 4H).

(*Received in Japan* 1 *February* 1995; *revised* 13 *March* 1995; *accepted* 18 *May* 1995)