Pergamon

Tetrahedron Letters 41 (2000) 1867–1869

TETRAHEDRON LETTERS

A convenient synthesis of 4-phenylchalcogeno allenic esters from α-(phenylchalcogeno)acid chlorides

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Received 13 December 1999; accepted 10 January 2000

Abstract

The reaction of ethyl 2-(triphenylphosphoranylidene) acetate or propionate **3a**–**b** with α-chalcogeno ketenes generated in situ by the reaction of α-chalcogeno acid chlorides **1**–**2** with triethylamine in dichloromethane gives moderate to good yields of 4-phenylchalcogeno allenic esters **4**. The corresponding 4-phenylseleno allenic esters **4a**–**e** were obtained in isolated yields of 60 to 93%, while 4-phenylthio allenic esters **4f**–**j** were obtained in isolated yields of 74 to 93%.

Keywords: allenes; selenium and compounds; sulfur compounds; Wittig reactions; phosphoranes.

Allenes have been widely used as building blocks in organic chemistry.[1] Among many methods available to prepare this class of compounds, the Wittig and the Horner reactions are particularly interesting for the construction of carbon–carbon double bonds, most notably because they allow controlling olefin regio- and stereochemistry.[2] In the synthesis of allenes, the reaction of ketenes (or carboxylic acid chlorides) with carbalkoxy methylidene triphenylphosphoranes or carbalkoxy diethyl phosphonate is very useful.[3] This route gives access to carbalkoxy allenes, a useful moiety for further transformations. To our knowledge, this route has not been completely explored for the synthesis of allenes with the synthetically useful organosulfur or organoselenium[4] and ester substituents. These compounds are useful as multifunctional building blocks, combining the versatile chalcogeno and the ester functionalities with the high and unique reactivity of allenes.[1,5]

In view of our continued interest in the synthesis of vinylic chalcogenides by Wittig-type reactions,[6] we decided to explore the easily accessible carboxy phosphoranes **3** (**3a** R^1=H; **3b** R^1=Me) in order to obtain 4-phenylchalcogeno allenic esters **4** (Scheme 1)**.** The reaction involves the treatment of ethyl 2-(triphenylphosphoranylidene) acetate or propionate **3a**–**b** with α-chalcogeno ketenes generated in situ by the reaction of α-chalcogeno acid chlorides **1**–**2** with triethylamine in dichloromethane solution, according to a procedure previously described.[3d] Some typical results are summarized in Table 1.

The reactions generally proceeded with very good yields of the desired products. They show a good generality, working well for both phosphoranes **3a** and **3b** as well as with six different acid chlorides,

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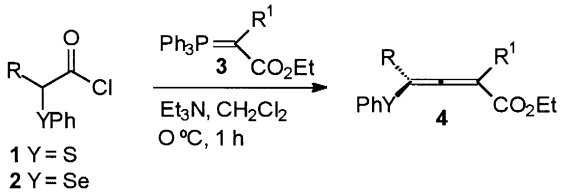
0040-4039/00/$ - see front matter
PII: S0040-4039(00)00067-8



Scheme 1.

Table 1
4-Phenylchalcogeno substituted allenic carboxylic esters prepared by the Wittig reaction

Product	Y	R	R^1	Yield[a], %	Product	Y	R	R^1	Yield[a], %
4a	Se	H	Me	78[b]	**4f**	S	H	Me	74[b]
4b	Se	Me	H	98 (93)[c]	**4g**	S	Me	Me	98 (93)[c]
4c	Se	Me	Me	97 (90)[c]	**4h**	S	Me	H	98 (93)[c]
4d	Se	*n*-Bu	H	94 (87)[c]	**4i**	S	*n*-Bu	Me	89 (85)[c]
4e	Se	*n*-Bu	Me	68 (60)[c]	**4j**	S	*n*-Bu	H	87 (83)[c]

[a] Yield of crude product (almost pure by ^{1}H NMR).
[b] Product not stable for purification by column chromatography.
[c] Isolated yields after column chromatography.

three with sulfur and three with selenium. Experimentally it was observed that the reactions were very fast at 0°C, and they were usually completed within 10 min, but in all cases for convenience they were worked-up only after 1 h, with no adverse effect of the longer reaction time. Simple extraction from the crude mixture with petroleum ether furnished the almost pure products by ^{1}H and ^{13}C NMR analysis, usually contaminated with small amounts of triphenylphosphinoxide. Whenever possible, the products were purified by column chromatography or Kugelrohr distillation. Of all examples studied allenes **4a** and **4f** proved to be the most labile and unstable during column chromatography purification on silica gel. Thus, they were obtained in reasonable purity as analyzed by TLC and ^{1}H NMR by extraction from the crude reaction mixture. All other examples could be purified by silica gel column chromatography. For all compounds **4** an absorption band near 1950 cm^{-1} assignable to the allenic function was observed in the IR spectra; the signal, due to the central carbon atom of the allene, appears near 205–210 ppm in the ^{13}C NMR spectra.

The α-phenylchalcogeno acid chlorides[7,8c] used in this work were easily accessible from the corresponding α-phenylchalcogeno acids by the reaction with thionyl chloride in CCl_4, followed by Kugelrohr distillation. To obtain the allenes **4a**–**g** in a good purity it was crucial to use the acid chlorides freshly distilled, since they decompose on storage. The only previously described synthetic application of alkylphenylseleno ketenes involves a [2+2] cycloaddition with imines to give the corresponding β-lactams,[7] while the sulfur derivatives have been applied to the synthesis of β-lactams and cyclobutanones.[8]

In summary, we have developed a very convenient method for the preparation of 4-phenylchalcogeno allenic ethyl esters[9,10] by generating α-phenylchalcogeno ketenes in situ from α-phenylchalcogeno acid chlorides and by treating this species with carboxyphosphoranes.

Acknowledgements

The authors thank the following agencies for financial support: FAPERGS, CNPq and CAPES. Special thanks are due to Prof. L. Wessjohann for revision of this manuscript.

References

1. (a) Schuster, H.; Coppola, G. *Allenes in Organic Synthesis*; John Wiley & Sons: New York, 1984. (b) Patai, S., Ed. *The Chemistry of Ketenes, Allenes, and Related Compounds, Parts 1 and 2*; Wiley-Interscience: New York, 1980. (c) Roberts, S. M., Ed. *Comprehensive Organic Functional Group Transformations*, Katritzky, A. R.; Meth-Cohn, O.; Rees, C. W., Eds.; Pergamon Press: Cambridge, 1995; Vol. 1.
2. (a) Cadogan, J. I. G., Ed. *Organophosphorus Reagents in Organic Synthesis*; Academic Press: London, 1979. (b) Maryanoff, B. E.; Reitz, A. B. *Chem. Ber.* **1989**, *89*, 863. (c) Kolodiazhnyi, O. I. *Russ. Chem. Rev.* **1997**, *66*, 225.
3. (a)Wadsworth, W. S.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1733. (b) Wittig, G.; Haag, A. *Chem. Ber.* **1963**, *96*, 1535. (c) Bestmann, H. J.; Hartung, H. *Chem. Ber.* **1966**, *99*, 1198. (d) Lang, R. W.; Hansen, H. J. *Helv. Chim. Acta* **1980**, *63*, 438. (e) Gilman, H.; Tomasi, R. A. *J. Org. Chem.* **1962**, *27*, 3647. (f) Kresze, G.; Runge, W.; Ruch, E. *Liebigs Ann. Chem.* **1972**, *756*, 112. (g) Runge, W.; Kresze, G. *Liebigs Ann. Chem.* **1975**, 1361. (h) Ibrahim-Ouali, M.; Sinibaldi, M. E.; Troin, Y.; Gardette, D.; Gramain, J. C. *Synth. Commun.* **1997**, *27*, 1827. (i) Marshall, J. A.; Wolf, M. A.; Wallace, E. M. *J. Org. Chem.* **1997**, *62*, 367.
4. Wessjohann, L. A.; Sinks, U. *J. prakt. Chem.* **1998**, *340*, 189. Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, 373. Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon: Oxford, 1986.
5. For some recent references, see: Engler, T. A.; Agrios, K.; Reddy, J. P.; Iyengar, R. *Tetrahedron Lett.* **1996**, *37*, 327. Shimizu, T.; Sakamaki, K.; Kamigata, N. *Tetrahedron Lett.* **1997**, *38*, 8529. Ma, S.; Wei, Q. *J. Org. Chem.* **1998**, *63*, 6387. Ma, S., Shi, Z.; Li, L. *J. Org. Chem.* **1998**, *63*, 4522. Ma, S.; Wei, Q. *J. Org. Chem.* **1999**, *64*, 1026.
6. Silveira, C. C.; Perin, G.; Braga, A. L.; Dabdoub, M. J.; Jacob, R. G. *Tetrahedron* **1999,** *55*, 7421 and references cited therein.
7. Agawa, T.; Ishida, M.; Ohshiro, Y. *Synthesis* **1980**, 933.
8. (a) Ishida, M.; Minami, T.; Agawa, T. *J. Org. Chem.* **1979**, *44*, 2067. (b) Palomo, C.; Cossio, F. P.; Odriozola, J. M.; Oiarbide, M.; Ontoria, J. M. *Tetrahedron Lett.* **1989**, *30*, 4577. (c) Minami, T.; Ishida, M.; Agawa, T. *J. Chem. Soc., Chem. Commun.* **1978**, 13.
9. Methyl 4-ethylsulfanyl-2,3-butadienoate has been recently described as a not isolated intermediate, obtained from 4-ethylthio-2-butynoate: Waizumi, N.; Itoh, T.; Fukuyama, T. *Tetrahedron Lett.* **1998**, *39*, 6015. Methyl 4-phenylselenopenta-2,3-dienoate: Brown, R. F. C.; Coulston, K. J.; Eastwood, F. W.; Hill, M. P. *Aust. J. Chem.* **1988**, *41*, 215.
10. General procedure for the preparation of allenes (**4**): To a solution of the phosphorane (1 mmol) in CH_2Cl_2 (5 mL) cooled to 0°C triethylamine (0.16 mL; 1.2 mmol) and a solution of the acid chloride (1.2 mmol) in CH_2Cl_2 (2 mL) were added. The reaction mixture was stirred at 0°C for 1 h, dissolved in CH_2Cl_2 (50 mL) and washed with water (50 mL). The organic phase was dried ($MgSO_4$), and the solvent removed under vacuum. The crude material was extracted several times with petroleum ether, and the solvent was removed to give the crude allene, almost pure by TLC and ^{1}H NMR. Whenever possible, the product was purified by silica gel column chromatography. Selected spectral data: Ethyl 2-methyl-4-phenylselanyl-2,3-butadienoate (**4a**): IR (neat) 1944 (C=C=C), 1710 (C=O) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.10–7.60 (m, 5H), 6.23 (q, *J*=2.4 Hz, 1H), 4.11 (q, *J*=7.0 Hz, 2H), 1.77 (d, *J*=2.4 Hz, 3H), 1.25 (d, *J*=7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 207.12 (C=*C*=C), 166.47 (C=O); MS *m/z* 282 (M^+), 128 (100%). Anal. calcd for $C_{13}H_{14}O_2Se$: C, 55.52; H, 5.02. Found: C, 55.27; H, 4.87. Ethyl 4-phenylselanyl-2,3-octadienoate (**4d**): IR (neat) 1952 (C=C=C), 1717 (C=O) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.10–7.60 (m, 5H), 5.39 (t, *J*=2.8 Hz, 1H), 4.18 (q, *J*=7.2 Hz, 2H), 2.31 (dt, *J*=7.1 and 2.8 Hz, 2H), 1.25–1.60 (m, 4H), 1.26 (t, *J*=7.2 Hz, 3H), 0.86 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 207.26 (C=*C*=C), 165.63 (C=O); MS *m/z* 324 (M^+), 281, 253, 235, 167, 157, 97, 77 (100%). Anal. calcd for $C_{l6}H_{20}O_2Se$: C, 59.44; H, 6.24. Found: C, 59.27; H, 6.32. Ethyl 2-methyl-4-phenylsulfanyl-2,3-pentadienoate (**4g**): IR (neat) 1954 (C=C=C), 1714 (C=O) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.20–7.50 (m, 5H), 4.0–4.25 (m, 2H), 2.00 (s, 3H), 1.75 (s, 3H), 1.31 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.07 (C=*C*=C), 166.94 (C=O); MS *m/z* 248 (M^+), 175 (100%). Anal. calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49. Found: C, 67.45; H, 6.58. Ethyl 2-methyl-4-phenylsulfanyl-2,3-octadienoate (**4i**): IR (neat) 1952 (C=C=C), 1713 (C=O) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.23–7.47 (m, 5H), 4.16 (q, *J*=7.2 Hz, 2H), 2.26 (t, *J*=7.1 Hz, 2H), 1.75 (s, 3H), 1.25–1.60 (m, 4H), 1.28 (t, *J*=7.2 Hz, 3H), 0.88 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.06 (C=*C*=C), 167.25 (C=O); MS *m/z* 290 (M^+), 261, 217, 181, 139, 111, 65 (100%). Anal. calcd for $C_{17}H_{22}O_2S$: C, 70.31; H, 7.64. Found: C, 69.94; H, 7.61.