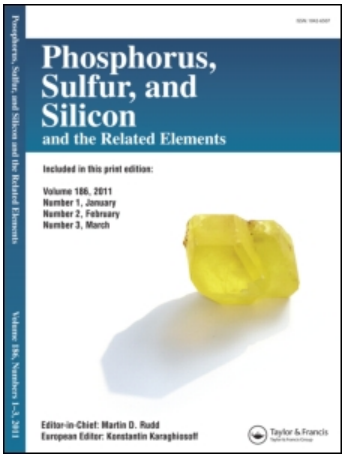


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Triphenylphosphine-Catalyzed Synthesis of Stable, Functionalized 2H-Oxetes

Sakineh Asghari[a]; Ahmad Khabbazi Habibi[a]
[a] Chemistry Department, Mazandaran University, Babolsar, Iran

To cite this Article Asghari, Sakineh and Habibi, Ahmad Khabbazi(2005) 'Triphenylphosphine-Catalyzed Synthesis of Stable, Functionalized 2H-Oxetes', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 11, 2451 — 2456
To link to this Article: DOI: 10.1080/104265090921182
URL: http://dx.doi.org/10.1080/104265090921182

Phosphorus, Sulfur, and Silicon, 180:2451–2456, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090921182

Taylor & Francis
Taylor & Francis Group

Triphenylphosphine-Catalyzed Synthesis of Stable, Functionalized 2H-Oxetes

Sakineh Asghari
Ahmad Khabbazi Habibi
Chemistry Department, Mazandaran University, Babolsar, Iran

Triphenylphosphine underwent Michael addition to dialkyl acetylenedicarboxylate and subsequently to the carbonyl group of α-haloketones. Then, these compounds were cyclized to produce the unstable 1,3-diionicphosphorus compound, which spontaneously lost triphenyl phosphine, and was converted to the functionalized oxetes derivatives.

Keywords α-Haloketones; triphenylphosphine; acetylenic ester; 2H-oxetes

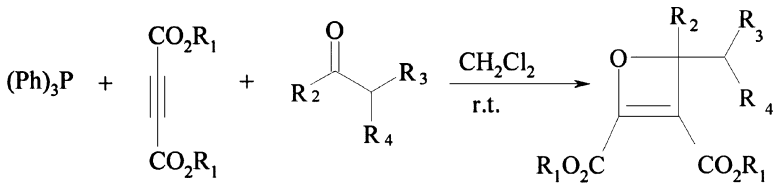
INTRODUCTION

Monocyclic four-membered heterocycles containing a double bond such as *2H*-oxetes are, in general, unstable. This is in part due to their tendency to undergo an electrocyclic ring opening to heterodynes.[1,2] As part of our current studies on the development of new routes to heterocyclic and carboxylic systems,[3,4] we now report a facile synthesis of the stable functionalized *2H*-oxetes. Reaction of α-haloketones, such as phenacyl chloride or 1,1-dichloroacetone **2** with dialkyl acetylenedicarboxylate **1** in the presence of triphenylphosphine, leads to the formation of the stable *2H*-oxetes ring systemes **3a–d** (Scheme 1).

RESULTS AND DISCUSSION

We know that the one-step [2+2] cycloaddition reaction between two unsaturated moieties is difficult and under vigorous conditions may occur stepwise *via* diradicals, and not in a concerted fusion. We report here a cycloaddition reaction between a carbonyl group of α-haloketone and acetylenic ester in the presence of triphenylphosphine as a catalyst that produces the stable *2H*-oxete in fairly high yields.

Received September 24, 2004; accepted October 26, 2004.
Address correspondence to Sakineh Asghari, Mazandaran University, Chemistry Department, PO Box 453, Babolsar, Iran. E-mail: s.asghari@umz.ac.ir



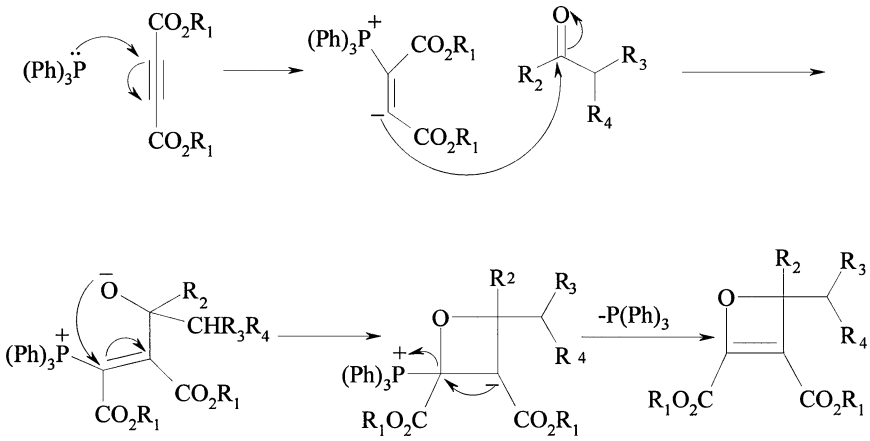
3	R_1	R_2	R_3	R_4	Yield (%)
a	CH_3	C_6H_5	H	Cl	80
b	C_2H_5	C_6H_5	H	Cl	72
c	CH_3	CH_3	Cl	Cl	70
d	C_2H_5	CH_3	Cl	Cl	74

SCHEME 1

Because this reaction did not take place in the absence of triphenylphosphine, it can be said that triphenylphosphine plays an important role as a catalyst for this reaction. It also is important to point out that this reaction between acetylenic ester and the unsubstituted ketone such as acetophenone did not take place; therefore, we can conclude that the existence of an electron-withdrawing substituent such as a chlorine atom is essential for this reaction.

The α-haloketones are among the most versatile intermediates in organic synthesis and their high reactivity makes them prone to react with a large number of nucleophiles to provide a variety of useful compounds.[5] On the basis of chemistry of trivalent phosphorus nucleophiles,[6–9] it is reasonable to assume that *2H*-oxetes result from an initial addition of triphenylphosphine to acetylenic esters and is subsequent to the carbonyl group of α-haloketone. The negatively charged oxygen atom attacks to an electeron-deficient olefinic carbon atom to produce the oxetane salt and subsequent loss of triphenylphosphine, which gives the stable functionalized *2H*-oxete **3** (Scheme 2).

The structure of **3a–d** was deduced from IR, ^{1}H, and ^{13}C NMR and mass spectra. The ^{1}H NMR spectrum of **3a** exhibited an AB quartet system at about 4.22 and 4.62 ppm for the CH_2Cl group because this compound possesses one stereogenic center and also two singlets at about 3.80 and 4.24 for two methoxy groups. The ^{13}C NMR spectrum of **3a** displayed two signals at about 123.02 and 149.56 for two olefinic carbon atoms of the *2H*-oxete ring, a signal at about 47.93 for the CH_2Cl group and a signal at about 85.57 for the aliphatic carbon atom of the



SCHEME 2

2H-oxete ring. The mass spectrum of **3a** exhibited molecular ion peaks at m/z 297(M^++1) (3%) and 299 (M^++3) (1%) because of the existence of the isotopes of the chlorine atom (^{35}Cl and ^{37}Cl). Initial fragmentations involved a loss from or complete loss of the side chains of the *2H*-oxete ring system.

The ^1H and ^{13}C NMR spectra and the fragmentations of the mass spectrum of **3b** are similar to those of **3a**, except for the ester groups.

The ^1H NMR spectrume of **3c** exhibited a singlet at about 1.82 ppm for the CH_3 group, two singlets at about 3.86 and 4.31 for two methoxy groups, and a singlet at about 6.30 for the $CHCl_2$ group. The ^{13}C NMR spectrum of **3c** displayed a signal at about 22.19 for CH_3, two signals 52.55 and 59.96 for two methoxy groups, and two signals at about 123.02 and 149.43 for two olefinic carbons. The mass spectra of **3c** displayed molecular ion peaks at m/z 268 (M^+) (53%), 270 (M^++2) (34%), 272 (M^++4) (6%), which confirm the existence of two chlorine atoms in the structure of **3c**.

The structure assignments made on the basis of NMR spectra of compounds **3a–d** were supported by measurement of their IR spectra. Of special interest are the strong carbonyl absorption bonds at 1771 and 1697 cm^{-1}.

In conclusion, we have developed a facile and efficient route for the synthsis of the stable *2H*-oxetes using electron-deficient ketones and acetylenic esters in the presence of triphenylphosphine as a catalysis. This procedure has as advantages a good yield, a mild reaction condition, the formation of cleaner products, and simple experimental and work-up conditions.

EXPERIMENTAL SECTION

Dialkyl acetylenedicarboxylates, triphenylphosphine, phenacyl chlorid, and 1,1-dichloroacetone were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were measured on an Electerothermal 9100 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with BRUKER DRX-500 AVANCE spectrometer at 500 and 125.8 MHz, respectively. Mass spectra were recorded on a Finnigan Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a IR-470 spectrometer.

Preparation of Dimethyl-2-(chloromethyl)-2-phenyl-2H-oxete-3,4-dicarboxylate (3a): General Procedure

To a magnetically stirred solution of phenacyl chloride (0.3 g, 2 mmol) and triphenylphosphine (0.52 g, 2 mmol) in CH_2Cl_2 (10 mL) was added, dropwise, to a mixture of dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) in CH_2Cl_2 (4 mL) at -10°C over 10 min. The mixture was allowed to stand at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was purified by silica gel (Merck silica gel, 230–400 mesh) column chromatography using hexane:ethyl acetate (80:20) as an eluent. The solvent was removed under reduced pressure and compound **3a** (0.47 g, m.p. 90°C, yield 80%) was obtained as a white powder. IR (KBr) (ν_{max}, cm^{-1}): 1771 and 1697 (C=O), 1648 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.80 (3H, s, OMe), 4.22 and 4.62 (2H, AB quartet, CH_2Cl), 4.24 (3H, s, OMe), 7.35–7.40 (5H, m, C_6H_5); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 47.93 (CH_2Cl), 52.38 and 60.01 (2 OMe), 85.57 (O—C—ph), 123.02 and 149.56 (olefinic carbons), 125.85, 128.91, 129.62 and 136.07 (aromatic carbons), 161.93 and 165.12 (2 C=O); MS, m/z (%): 297 (M^++1) (3), 299 (M^++3) (1), 281 (M^+−Me) (1.5), 283 (M^++2, −Me) (0.5), 265 (M^+, —OMe) (9), 267 (M^++2, —OMe) (3), 247 (M^+ —CH_2Cl) (100), 105 [M^+ —(CH_2Cl + MeO_2C—C=C—CO_2Me)] (67), 77(C_6H_5) (29).

Diethyl-2-(chloromethyl)-2-phenyl-2H-oxete-3,4-dicarboxylate (3b)

White powder, m.p. 46°C, yield 72%, IR (KBr) (ν_{max}, cm^{-1}): 1773 and 1692 (C=O), 1646 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.24 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 1.37 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 4.16–4.28 (2H, m, OCH_2), 4.22 and 4.61 (2H, AB quartet, CH_2Cl), 4.5–1.74 (2H, m, OCH_2); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 13.99 and 15.50 (2 CH_3),

48.05 (CH_2Cl), 61.48 and 68.62 (2 OCH_2), 85.62 (O—C—ph), 124.10 and 149.20 (olefinic carbons), 125.80, 128.84, 129.36 and 136.20 (aromatic carbons), 161.50 and 165.44 (2C=O); MS, *m*/*z* (%): 325 (M^++1) (39), 327 (M^++3) (12), 275 (M^+—CH_2Cl) (100), 219 [M^+,—(CH_2Cl + $2C_2H_4$)] (32), 105 [M^+, —(CH_2Cl + MeO_2C—C=C—CO_2Me)] (76).

Dimethyl-2-(dichloromethyl)-2-methyl-2H-oxete-3,4-dicarboxylate (3c)

White powder, m.p. 83°C, yield 70%, IR (KBr) (ν_{max}, cm^{-1}): 1776 and 1704 (C=O), 1646 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.82 (3H, s, CH_3), 3.86 and 4.31 (6H, 2s, $2OCH_3$), 6.30 (1H, s, $CHCl_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 22.19 (CH_3), 52.55 and 59.96 ($2OCH_3$), 89.16 [O—C(CH_3) ($CHCl_2$)], 74.52 ($CHCl_2$), 123.02 and 149.43 (olefinic carbons), 161.58 and 164.62 (2 C=O); MS, *m*/*z* (%): 269 (M^++1) (52), 271 (M^++3) (34), 273 (M^++5) (6), 273 (M^+—MeOH) (15), 239 (M^++2-MeOH) (10), 241 (M^++4-MeOH) (1.7), 185 (M^+-$CHCl_2$) (100), 153 [(M^+—($CHCl_2$ + MeOH)] (36).

Diethyl-2-(dichloromethyl)-2-methyl-2H-oxete-3,4-dicarboxylate (3d)

White powder, m.p. 50°C, yield 74%, IR (KBr) (ν_{max}, cm^{-1}): 1779 and 1693 (C=O), 1643 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.31 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 1.35 (3H, t, $^3J_{HH}$ 7 Hz, CH_3), 1.76 (3H, s, CH_3), 4.27 (2H, q, J_{HH} 7 Hz, OCH_2), 4.5–4.72 (2H, m, OCH_2), 6.25 (1H, s, $CHCl_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$): δC 14.08 and 15.53 ($2CH_3$), 22.22 (CH_3), 61.71 and 68.64 ($2OCH_2$), 74.62 ($CHCl_2$), 85.32 [O—C(CH_3) ($CHCl_2$)], 123.99 and 149.16 (olefinic carbons), 161.24 and 164.93 (2 C=O); MS, *m*/*z* (%): 297 (M^++1) (35), 299 (M^++3) (24), 301 (M^++5) (4), 251 (M^+—MeOH) (18), 253 (M^+ + 2—MeOH) (12), 255 (M^++4—MeOH) (12), 213 (M^+—$CHCl_2$) (100), 185 [M^+ —($CHCl_2$ + C_2H_4)] (41), 157 [M^+—($CHCl_2$ + $2C_2H_4$)] (86).

REFERENCES

[1] P. C. Martino and P. B. Sherlin, *J. Am. Chem. Soc.*, **102,** 5249 (1980).
[2] L. E. Friedrich and P. Y. Lam, *J. Org. Chem.*, **46,** 306 (1981).
[3] I. Yavari and S. Asghari, *Tetrahedron*, **55,** 11853 (1999); I. Yavari and R. Baharfar, *Tetrahedron Lett.*, **38,** 4259 (1997).
[4] I. Yavari and M. Bayat, *Tetrahedron*, **59,** 2001 (2003).
[5] N. Kimpe and R. Verhe, In *The Chemistry of α-Haloketones α-Haloaldehydes and α-Haloimines*, S. Patai and Z. Rapport, Eds. (Chicgester, UK: John Willey, 1988), pp. 1–119.

[6] D. E. C. Corbridge, *Phosphorus: An Outline of Its Chemistry, Biochemistry and Technology* (Elsevier, 1995), pp. 42–47.
[7] O. I. Kolodiazhynyi, *Russ. Chem. Rev.*, **66,** 225 (1997).
[8] R. A. Cherkosov and M. A. Pudovik, *Russ. Chem. Rev.*, **63,** 1019 (1994).
[9] K. M. Pietrusrewtz and M. Zablocka, *Chem. Rev.*, **109,** 83 (1983).