Short communication

Synthesis of Functionalized Stable Phosphorus Ylides. New Synthesis of Dimethyl (Z)-2-[2-(ethoxycarbonyl)-1-cyclopentenyl]-2-butenedioates

Sakineh Asghari,* Zahra Sobhaninia and Zahra Naderi

Department of Chemistry, University of Mazandaran, P. O. BOX 453, Babolsar, Iran

* Corresponding author: E-mail: s.asghari@umz.ac.ir, Fax: 00981125233702

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Abstract

Ethyl 2-oxo-1-cyclopentanecarboxylate undergoes a reaction with dialkyl acetylenedicarboxylate in the presence of triphenylphosphine to produce stable phosphorus ylides in good yields. These ylides undergo intramolecular Wittig reaction in boiling toluene to produce cyclobutene derivatives, which undergo ring-opening reactions to produce dialkyl (Z)-2-[2-(ethoxycarbonyl)-1-cyclopentenyl]-2-butenedioates.

Keywords: Ethyl 2-oxo-1-cyclopentanecarboxylate, dialkyl acetylenedicarboxylate, triphenylphosphine, intramolecular Wittig reaction.

1. Introduction

Organophosphorus compounds, those bearing a carbon atom directly bonded to a phosphorus atom are synthetic targets of interest, at least because of their value for a variety of industrial, biological, and chemical synthetic uses.1–3 Phosphorus ylides are reactive systems, which take part in many valuable reactions in the synthesis of organic products.4–6 We previously reported the synthesis of cyclobutene derivatives by intramolecular Wittig reaction, which were converted to electron-deficient 1,3-dienes.7–9 In continuation of studies in introducing the new methods on synthesis of phosphorus ylide and electron-deficient compounds, we wish to report the reaction between ethyl 2-oxo-1-cyclopentanecarboxylate 2 and dialkyl acetylenedicarboxylates in the presence of triphenylphosphine. Thus, reaction of triphenylphosphine with electron-deficient acetylenic ester 1 in the presence of a CH-acid such as 2 leads to ylide 3 in good yields.

These compounds then undergo intramolecular Wittig reaction in boiling toluene to produce cyclobutene derivatives 4, which undergo electrocyclic ring-opening reaction to generate highly functionalized 1,3-dienes 5 (Scheme 1).

2. Results and Discussion

On the basis of the chemistry of trivalent phosphorus nucleophiles,10,11 it is reasonable to assume that ylide 3 results from initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by 2, followed by attack of the carbon atom of the anion of 2 to vinyltriphenylphosphonium cation 6 to generate the stable ylide 3. This compound undergoes intramolecular Wittig reaction in boiling toluene to produce strained cyclobutene derivative 4, which is finally converted to electron-deficient 1,3 – dienes 5 via a ring-opening reaction (Scheme 2).

The structures of compounds 3a–c were deduced from IR, 1H and 13C NMR spectra. The mass spectra of these ylides are fairly similar and display the molecular ion peaks. Other fragmentations involved the loss of the ester moieties or PPh3 from the ion molecule. Although compounds 3 possesses two stereogenic centers, and two diastereomers are expected, the 1H NMR spectrum of the reaction mixture shows only one diastereoisomer.

The 1H and 13C NMR spectra of 3a–c are also consistent with the presence of two isomers (see experimental section). The ylide moiety of these compounds is strongly conjugated to the adjacent carbonyl group and its rotation...
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13C NMR and IR spectral data. The strong carbonyl absorption bands at 1722–1735 cm⁻¹ for all the compounds were observed. The 1H NMR spectrum of 5a displays characteristic signals at about 6.75 ppm for the CH group and appropriate chemical shifts in the olefinic region. Because of loss of the chiral center during the conversion of compound 3 to 5, the proton signals of CH₂ groups were simplified in 5. The 13C NMR spectrum of 5a exhibits four signals at about 126.1, 132.0, 144.1 and 149.7 ppm for olefinic carbons. The partial assignment of these signals is given in experimental section. The mass spectra of the compound 5a displayed molecular ion peak at m/z = 282. Initial fragmentations involve loss of the alkoxy and esteric groups.

3. Experimental

Ethyl 2-oxo-1-cyclopentanecarboxylate, dialkyl acetylenedicarboxylate and triphenyl phosphine were obtained from Fluka (Buchs, Switzerland) and used without further purifications. Melting points were measured with an Electrothermal 9100 apparatus. 1H, 13C and 31P NMR spectra were measured at 500.1, 125.8, and 202.5 MHz, respectively, with a Bruker DRX-500 Avance instrument. CDCl₃ was used as solvent. IR spectra were recorded on a Shimadzu FT-IR Bruker Vector 22 spectrometer. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

**General procedure for preparation of dialkyl 2-[1-(ethoxycarbonyl)-2-oxocyclopentyl]-3-(1,1,1-triphenyl-L₅-phosphanylidene)succinate compounds (examplified by 3a).**

To a magnetically stirred solution of ethyl 2-oxo-1-cyclopentane carboxylate (0.31 g, 2 mmol) and triphenylphosphine (0.52 g, 2 mmol) in CH₂Cl₂ (10 ml) was added, dropwise, a mixture of dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) in CH₂Cl₂ (3 ml) at −10 °C over 10 min. The mixture was allowed to stand at room temperature for 24 hours. 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 (1:5) as eluent. The solvent was removed under reduced pressure and ylide 3a was obtained.

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Diethyl 2-[(ethoxycarbonyl)-2-oxocyclopentyl]-3-(1,1,1-triphenyl-α-phosphanylidene) succinate (3b): White powder, m.p. 160–162 °C, yield 0.9 g (75%); IR (KBr) (ν max cm−1): 3040 (CH), 2982 (CH), 1745, 1726 (C=O), 1645 (C=C); MS, m/z (%): 279 (OPPh3+1), 10, 262 (OPPh2, 2), 180 [M=–(PPh2+2CO,Et), 100], 86 (CHCO,Et+, 100), 57 (CH3CHO,CHO-C, 36); Anal. Calcld for C34H37O7P (588.64): C, 69.38; H, 6.34; Found: C, 69.32; H, 6.30.

Major isomer, 3a-(Z) (68%), 1H NMR (500.1 MHz, CDCl3): δ 1.03 (3H, t, J ph 7.1 Hz, CH3), 1.74–1.84 (4H, m, 2CH2), 2.32–2.4 and 2.55–2.62 (2H, 2m, CH2), 3.46 (d, 3J ph 18.8 Hz, CH), 3.64 (3H, s, OCH3), 3.67–3.83 (2H, m, OCH2), 7.43–7.53 (15H, m, arom); 13C NMR (125.8 MHz, CDCl3): δ 13.9 (CH3), 20.35 (CH2), 28.3 (CMe3), 48.2 (d, Jpc 14.1 Hz, CH), 49.5 and 51.6 (2OCH2), 61.1 (OCH2), 67.1 (quaternary carbon of cyclopentanone), 127.1 (d, Jpc 11.7 Hz, C ipso), 128.4 (d, Jpc 11 Hz, C met), 132.0 (C para), 134.0 (d, Jpc 9.6 Hz, C ortho), 169.1 (C=O, ester), 170.4 (d, Jpc 6.5 Hz, C=O ester), 213.5 (C=O, ketone); 31P NMR (202.5 MHz, CDCl3): δp 26.23.

Minor isomer, 3a-(E) (32%), 1H NMR (500.1 MHz, CDCl3): δ 1.17 (3H, t, J ph 7.1 Hz, CH3), 1.74–1.84 (4H, m, 2CH2), 2.32–2.4 and 2.55–2.62 (2H, 2m, CH2), 3.46 (d, 3J ph 18.8 Hz, CH), 3.64 (3H, s, OCH3), 3.67–3.83 (2H, m, OCH2), 7.43–7.53 (15H, m, arom); 13C NMR (125.8 MHz, CDCl3): δ 13.9 (CH3), 20.3, 30.6 and 36.8 (3CH2), 39.0 (d, Jpc 125.8 Hz, P=C), 48.4 and 51.7 (2OCH2), 49.1 (d, Jpc 13.7 Hz, CH), 60.9 (OCH2), 67.1 (quaternary carbon of cyclopentanone), 127.0 (d, Jpc 92.7 Hz, C ipso), 128.3 (d, Jpc 11.9 Hz, C met), 131.7 (C para), 133.9 (d, Jpc 9.6 Hz, C ortho), 169.2 (C=O, ester), 170.0 (d, Jpc 13.8 Hz, C=O ester), 174.6 (d, Jpc 6.5 Hz, C=O ester), 213.5 (C=O, ketone); 31P NMR (202.5 MHz, CDCl3): δp 26.23.
Di-tert-butyl(Z)-2-[2-(ethoxycarbonyl)-1-cyclopentenyl]-2-butenedioate (5c): Yellow oil, yield 0.14 g (40%); IR (KBr) (ν_{max} cm^{-1}): 1733, 1722 (C=O), 1635 (C=C); ¹H NMR (500 MHz, CDCl₃): δ_1 1.18 (3H, t, 3J_{HH} 7.1 Hz, CH₃), 1.25 (3H, t, 3J_{HH} 7.2 Hz, CH₃), 1.26 (3H, t, 3J_{HH} 7.1 Hz, CH₃), 2.01 (2H, quintet, 3J_{HH} 7.5 Hz, CH₂), 2.68–2.73 (4H, m, 2CH₂), 4.07 (2H, q, 3J_{HH} 7.1 Hz, OCH₂), 4.15 (2H, q, 3J_{HH} 7.1 Hz, OCH₂), 4.22 (2H, q, 3J_{HH} 7.1 Hz, OCH₂), 6.74 (1H, s, CH); ¹³C NMR (125.8 MHz, CDCl₃): δ_2 14.1 (CH₂), 14.1 (CH₂), 29.7, 33.2 and 39.0 (3CH₂), 60.2, 60.8 and 61.7 (3OCH₂), 126.4, 132.3, 144.0 and 149.9 (olefinic carbons), 164.7, 164.8 and 164.8 (3C=O, ester); MS m/z (%): 366 (M^+), 2, 310 (M^+–C₄H₈, 11), 265 (M^+–CO₂Bu, 2), 209 [M^+–(CO₂Bu+C₂H₄)], 181 [M^+–(CO₂Bu+C₂H₄+C₂H₆)], 57 (C₆H₅), 45; Anal. Calcd. for C₁₀H₁₇O₆ (366.46): C, 65.55; H, 8.25; Found: C, 65.49; H, 8.21.

4. Conclusion

The present method may be used as a practical route for the synthesis of stable phosphorous ylides, and as convenient preparation of functionalized 1,3-dienes using intramolecular Wittig reaction under neutral conditions. This procedure has advantages of high yields, mild reaction conditions, and simple experimental and work-up conditions.

5. References

**Povzetek**

Prispevek obravnava reakcijo etil 2-okso-1-ciklopentan karboksilatov z acetilendikarboksilati v prisotnosti trifenilfosfina. Pri tem nastanejo stabilni fosforjevi ilidi z dobrimi izkoristi. Tako pripravljeni ilidi pri refluku toluena v intramolekularni Wittigovi reakciji dajejo derivate ciklobutena, ki pri nadaljnjih reakcijah odpiranja obroča tvorijo dialkil (Z)-2-[2-(etoksikarbonil)-1-ciklopenteni]-2-butendioate.