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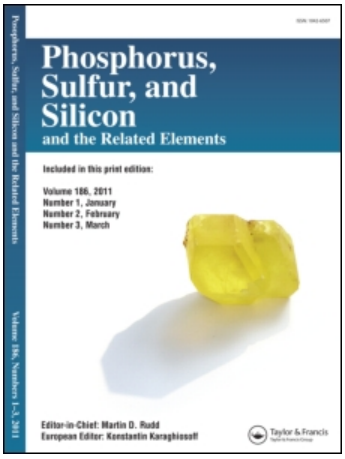

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ONE-POT SYNTHESIS OF 2-SUBSTUTUTED ALLENECARBOXYLATES

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2-Phosphoryl-(**2–4**), 2-sulfinyl-(**5**) and 2-sulfonyl-2,3-alkadienoates (**6** and **7**) were prepared in an one-pot reaction by a [2,3]-sigmatropic rearangement of the heteroatom-substituted 2-alkynoates obtained from ethyl propynoate and subsequent treatment with lithium diisopropylamide, ketone, trimethylchlorosilane and phosphorus- or sulfur-containing chloride.

Keywords: ethyl propynoate; phosphorus- or sulfur-containing chlorides; 2-phosphoryl-2,3-alkadienoates; 2-sulfinyl-2,3-alkadienoate; 2-sulfonyl-2,3-alkadienoates

INTRODUCTION

Reaction of propargyl alcohols with a halogen-containing reagent as sulfenyl halides[1] and sulfinyl chlorides[2] is a convenient method for the preparation of propargyl compounds (sulfenates or sulfinates) which usually undergo [2,3]-sigmatropic rearangement to allenic products[1–4] (sulfoxides or sulfones). On the other hand, the synthesis of alkyl 2,3-alkadienoates by Wittig reaction have been reported.[5] The synthesis of α-thioallenecarboxylates by metaleation of an allene sulfide, following by treatment with methyl chloroformiate was mentioned by H. G. Viehe[6a] without giving experimental details. An alternative route which enables the preparation of thio-,[6b] sulfinyl-[6b,6c] and sulfonyl-substituted[6b] allenecarboxylates starts from methyl 4-hydroxy-2-alkynoate.

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† *As short communication.*

As a part of our research program on the chemistry of the heteroatom-containing highly unsaturated compounds, we required[11] a convenient method to introduce phosphorus and sulfur functionalities in the α-position to the ester group of allenecarboxylates. The phosphoryl, sulfinyl and sulfonyl group attact increasing attention as useful functionalities in organic synthesis. Of particular interest are the applications of these groups as temporary transformers of chemical reactivity of the allenic system in the synthesis of eventually heterocyclic compounds.[4,7]

RESULTS AND DISCUSSION

Interaction of the lithio compounds **A**, generated *in situ* from ethyl propynoate (**1**) and lithium diisopropylamide, with acetone or cyclohexanone and subsequent treatment with trimethylchlorosilane and phosphorus-(dimethylchlorophosphite or diphenyl-chlorophosphine) or sulfur-containing (phenylsulfenyl-, trichloromethylsulfinyl- or methylsulfinyl-) chloride led to the 3-heteroatom-substituted 2-alkynoates **B**, which underwent a [2,3]-sigmatropic rearangement to the expected 2-phosphoryl(**2–4**), 2-sulfinyl- (**5**) or 2-sulfonyl-2,3-alkadienoates (**6** and **7**) respectively, according to the following reaction sequence outlined in the **Scheme**:

After a conventional work-up, the resulting 2-heteroatom-substituted 2,3-alkadienoates **2–7** were isolated by preparative TLC as light yellow oils (**2, 4** and **5**) or crystals (**3, 6** and **7**) in moderate yields (32–43 %) and identified by ^{1}H NMR and IR spectra as well as elemental analysis.

Further work is in progress to investigate the prepared compounds in electrophile-induced cyclization reactions.

EXPERIMENTAL

General Methods

^{1}H NMR spectra were obtained on a JEOL JNM-FX-60 spectrometer for solutions in $CDCl_3$ operating at 60 MHz. Chemical shifts are in parts per million downfield from internal TMS.

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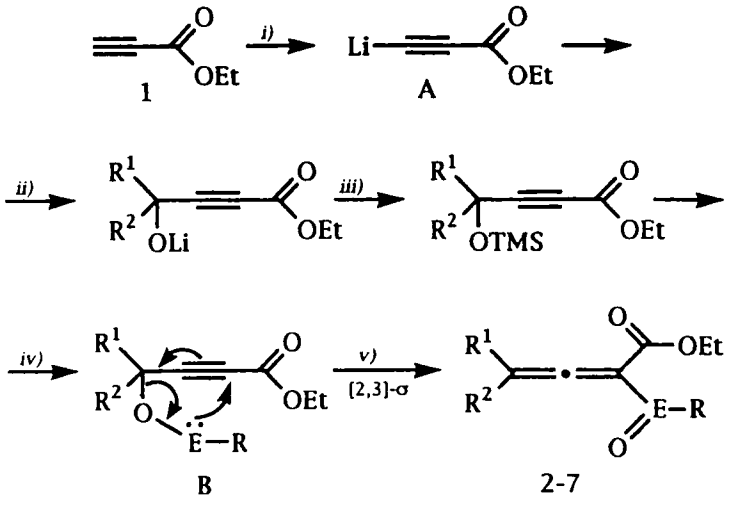

2-7	E	R	R^1	R^2
2	P-OMe	OMe	Me	Me
3	P-Ph	Ph	Me	Me
4	P-OMe	OMe	$-(CH_2)_5-$	
5	S	Ph	Me	Me
6	S=O	CCl_3	Me	Me
7	S=O	Me	$-(CH_2)_5-$	

Reagents and Conditions:

i) LDA, THF, -100 °C, 1 h;
ii) acetone (2, 3, 5, 6) or cyclohexanone (4 and 7), THF, -100 °C, 10 min;
iii) Me_3SiCl, THF, -100 °C to -10 °C, 10 min;
iv) $(MeO)_2PCl$ (2 and 4), Ph_2PCl (3), PhSCl (5), $CCl_3S(O)Cl$ (6) or MeS(O)Cl (7), THF, -10 °C to rt;
v) rt, 5 h (2, 3 and 4); THF, reflux, 2 h (5); toluene, reflux, 3 h (6 and 7).

SCHEME

IR spectra were recorded with an IR-72 spectrophotometer (Carl Zeiss, Jena). Elemental analyses were carried out by the University of Shoumen Microanalytical Service Laboratory.

The melting points were measured in open capillary tubes and are uncorrected. The solvents were purified by standard methods. The reactions were carried out in ovendried glassware under an argon atmosphere and exclusion of moisture. All compounds were checked for their purity on TLC plates.

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Starting materials

Dimethylchlorophosphite was synthesized from phosphorus trichloride and methanol according to the literature.[8] Phenylsulfenyl chloride was prepared from diphenyl disulfide and sulfuryl chloride at −20 °C and used after distillation.[9] Methylsulfinyl chloride was synthesized from dimethyl disulfide and sulfuryl chloride in glacial acetic acid and used after distillation.[10]

Synthesis of 2-substituted allenecarboxylates (2–7). General procedure

To a solution of lithium diisopropylamide (LDA), generated *in situ* from diisopropylamine (DIA) (1.11 g, 11 mmol) and n-butyl lithium (n-BuLi) (1.6 M in hexane, 6.25 ml, 10 mmol), in tetrahydrofuran (THF) (20 ml) was added dropwise a solution of ethyl propynoate (**1**) (10 mmol) in THF (10 ml) at −100 °C. The reaction mixture was stirred at this temperature for 1 h. After the addition of a solution of acetone (10 mmol) (for preparation of compounds **2, 3, 5** and **6**) or cyclohexanone (10 mmol) (for preparation of compounds **4** and **7**) in THF (20 ml) at −100 °C, the mixture was stirred at the same temperature for 10 min. Trimethylchlorosilane (10 mmol) in THF (10 ml) was added dropwise at −100 °C. After the addition was completed, the mixture was warmed to −10 °C and stirred at the same temperature for an additional 10 min. After that a solution of 10 mmol dimethylchlorophosphite (for preparation of compounds **2**and **4**), diphenylchlorophosphine (for preparation of compound **3**), phenylsulfenyl chloride (for preparation of compound **5**), trichloromethylsulfinyl chloride (for preparation of compound **6**) or methylsulfinyl chloride (for preparation of compound **7**) in THF (20 ml) was added dropwise to the reaction mixture at −10 °C. The mixture was stirred at room temperature or reflux for 2–5h, quenched with 2N HCl, extracted with ether or ethylacetate, washed with saturated NaCl, and dried over anhydrous sodium sulfate. In case of synthesis of compound **6** and **7**, the residue was dissolved in dry toluene and heated at reflux for 3h. After evaporation of the solvents, the residue was chromatographed on silica gel to give the pure 2-heteroatom-substituted allenecarboxylates **2–7** with moderate yields (32–43%).

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Ethyl 4-methyl-2-(dimethoxyphosphoryl)-2,3-pentadienoate (2)

The compound was prepared from the lithio derivative **A**, acetone, trimethylchlorosilane and dimethylchlorophosphite. [2,3]-Sigmatropic rearangement carried out in THF at room temperature for 5h. Eluent for preparative TLC: hexane: ethylacetate = 3:1. Oil, $C_{10}H_{17}O_5P$, Calcd., %: P 12.48; Found, %: P 12.56. IR spectra (neat), cm^{-1}; 1277 (P=O), 1705 (C=O), 1957 (C=C=C). ^1H NMR spectra ($CDCl_3$), δ: 1.37 (t, $^3J_{HH}$ 6.9 Hz, 3H, $\underline{Me}CH_2O$), 1.76 and 1.82 (s, s, 6H, 2Me), 3.76–4.37 (m, 2H, $MeCH_2O$), 3.57 (d, $^3J_{HP}$ 10.9 Hz, 6H, 2MeO).

Ethyl 4-methyl-2-(diphenylphosphoryl)-2,3-pentadienoate (3)

The compound was prepared from the lithio derivative **A**, acetone, trimethylchlorosilane and diphenylchlorophosphine. [2,3]-Sigmatropic rearangement carried out in THF at room temperature for 5h. Eluent for preparative TLC: hexane: ethylacetate = 4:1. Crystallization from heptane at −15°C furnishes **3** as white crystals. M.p. 85–86 °C, $C_{20}H_{21}O_3P$, Calcd., %: P 9.10; Found, %: P 9.18. IR spectra (nujol), cm^{-1}: 1159 (P=O), 1697 (C=O), 1952 (C=C=C). ^1H NMR spectra ($CDCl_3$), δ: 1.38 (t, $^3J_{HH}$ 7.0 Hz, 3H, $\underline{Me}CH_2O$), 1.74 and 1.79 (s, s, 6H, 2Me), 3.74–4.36 (m, 2H, $MeCH_2O$), 7.35–7.63 (m, 10H, Ph_2P).

Ethyl 2-(dimethoxyphosphoryl)-cyclohexylidene-propenoate (4)

The compound was prepared from the lithio derivative **A**, cyclohexanone, trimethylchlorosilane and dimethylchlorophosphite. [2,3]-Sigmatropic rearangement carried out in THF at room temperature for 5h. Eluent for preparative TLC: hexane: ethylacetate = 3:1. Oil, $C_{13}H_{21}O_5P$, Calcd., %: P 10.75; Found, %: P 10.64. IR spectra (neat), cm^{-1}: 1269 (P=O), 1703 (C=O), 1958 (C=C=C). ^1H NMR spectra ($CDCl_3$), δ: 1.36 (t, $^3J_{HH}$ 6.9 Hz, 3H, $\underline{Me}CH_2O$), 1.55 and 2.23 (s, s, 6H and 4H, cyclohexylidene), 3.55 (d, $^3J_{HP}$ 10.8 Hz, 6H, 2MeO), 3.72–4.38 (m, 2H, $MeCH_2O$).

Ethyl 4-methyl-2-(phenylsulfinyl)-2,3-pentadienoate (5)

The compound was prepared from the lithio derivative **A**, acetone, trimethylchlorosilane and phenylsulfenyl chloride. [2,3]-Sigmatropic

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rearangement carried out in THF at reflux for 2h. Eluent for preparative TLC: hexane:ethylacetate = 2:1. Crystallization from ether:hexane = 1:3 at −15 °C furnishes **5** as light yellow crystals. M.p. 104–105 °C. $C_{14}H_{16}O_3S$, Calcd., %: S 12.13; Found, %: S 12.16. IR spectra (nujol), cm^{-1}: 1054 (S=O), 1714 (C=O), 1952 (C=C=C). ^1H NMR spectra ($CDCl_3$), δ: 1.36 (t, $^3J_{HH}$ 6.9 Hz, 3H, $\underline{Me}CH_2O$), 1.73 and 1.79 (s, s, 6H, 2Me), 3.76–4.37 (m, 2H, $MeCH_2O$), 7.4–7.72 (m, 5H, Ph).

Ethyl 4-methyl-2-(trichloromethylsulfonyl)-2,3-pentadienoate (6)

The compound was prepared from the lithio derivative **A**, acetone, trimethylchlorosilane and trichloromethylsulfinyl chloride. [2,3]-Sigmatropic rearangement carried out in toluene at reflux for 3h. Eluent for preparative TLC: hexane:ethylacetate = 1:1. Crystallization from ether:hexane = 1:3 at −15 °C furnishes **6** as light yellow crystals. M.p. 91–92 °C. $C_9H_{11}O_4SCl_3$, Calcd., %: S 9.97, Cl 33.07; Found, %: S 10.06, Cl 32.94. IR spectra (nujol), cm^{-1}: 1146 and 1344 (SO_2), 1720 (C=O), 1956 (C=C=C). ^1H NMR spectra ($CDCl_3$), δ: 1.34 (t, $^3J_{HH}$ 6.7 Hz, 3H, $\underline{Me}CH_2O$), 1.94 (s, 6H, 2Me), 3.68–4.29 (m, 2H, $MeCH_2O$).

Ethyl 2-(methylsulfonyl)-cyclohexylidene-propenoate (8)

The compound was prepared from the lithio derivative **A**, cyclohexanone, trimethylchlorosilane and methylsulfinyl chloride. [2,3]-Sigmatropic rearangement carried out in toluene at reflux for 3.5h. Eluent for preparative TLC: hexane: ethylacetate = 1:1. Crystallization from ether:hexane = 1:3 at −15 °C furnishes **6** as light yellow crystals. M.p. 71–73 °C; $C_{12}H_{18}O_4S$, Calcd., %: S 12.41; Found, %: S 12.47. IR spectra (nujol), cm^{-1}: 1153 and 1348 (SO_2), 1711 (C=O), 1958 (C=C=C). ^1H NMR spectra ($CDCl_3$), δ: 1.38 (t, $^3J_{HH}$ 6.9 Hz, 3H, $\underline{Me}CH_2O$), 1.5 and 2.2 (s, s, 6H and 4H, cyclohexylidene), 3.18 (s, 3H, Me-SO_2) 3.74–4.18 (m, 2H, $MeCH_2O$).

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