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Simple method for preparation of Dialkyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonates.

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ABSTRACT: A simple synthesis of dialkyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonates from thiazolium salts and trialkyl phosphites was described. The series of dialkyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonates with various substituents in position 3, 4 and 5 of the thiazol ring were prepared. However only phosphonates with aryl on nitrogen atom were stable enough for chromatography purification, nevertheless all of these new phosphonates are very sensitive for oxidation. We made efforts to apply dialkyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonates in Horner-Wadsworth-Emmons reaction but the generated antiaromatic anion of phosphonate decomposed quickly even at -70°C.

INTRODUCTION

The tetraheterofulvalenes belong to a class compounds that are in the circle of interest of many laboratories from physics to organic chemistry. Their popularity is due to the great variety of applications of these compounds.

Most of the applications of tetraheterofulvalenes are as a result of their high electron donating properties; this group of compounds is usually an integral part of synthetic metals [1], semiconductors, and other advanced materials [2]. The majority of applied tetraheterofulvalenes contain four sulfur atoms or sulfur and selenium due to their

availability, relative oxidation stability and easy modification in side chain and also to possibility of preparing unsymmetrical tetrathiafulvalenes (TTF) [3].

Horner-Wadsworth-Emmons reaction is successfully used for the preparation of unsymmetrical tetrathiafulvalenes with high selectivity [4-7]. The Wittig reaction may also be used for the preparation of unsymmetrical tetrathiafulvalenes; however, with lower selectivity [8-10]. The aforementioned methods use 1,3-dithio-2-yl phosphonates esters or 1,3-dithio-2-yl phosphonium salts respectively as key intermediates.

However in recent years, there has been an interest in dithiadiazafulvalenes (DTDAFs) [11] as donor materials but research in this area is limited due to the low stability of DTDAFs, the lack of methods for modification of already prepared DTDAFs as well as a lack of a method for selective preparation of unsymmetrical dithiadiazafulvalenes [12].

It is not difficult to deduce the hypothesis that unsymmetrical dithiadiazafulvalenes **1** could be prepared by the route similar to the strategy used for the preparation of unsymmetrical TTF [4-10] (Scheme 1) by the coupling of dialkyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonates **2** and 2-piperidin-1,3-thiazolium salts or (2,3-dihydro-1,3-thiazol-2-yl)-phosphonium salts **3** and 1,3-thiazolium salts.

SCHEME 1

However it must be pointed that required key intermediates dialkyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonates **2** or (2,3-dihydro-1,3-thiazol-2-yl)-phosphonium salts **3** are not common compounds, with only three examples of these phosphonates described in the chemical literature. The first was published in 1967; Razumow [13] prepared (2,3-dihydro-benzothiazol-2-yl)-phosphonate in the reaction of *o*-aminothiophenol with dialkyl (dimethoxy)methylphosphonate. Takamizawa obtained a phosphonate derivative of thiamine

[14] in a multistep reaction. One example of (3-Methyl-2,3-dihydro-benzothiazol-2-yl)-phosphonate was also prepared in the cleavage of bis(3-methylthiazolidyn-2-ylidene) with diethyl phosphite [15].

Therefore we made an attempt to find an easy and efficient method for preparation of dialkyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonates **2.**

RESULTS AND DISCUSSION

It is well known that dithiadiazafulvalenes are very susceptible to oxidation by air oxygen [11]. Therefore for our research we needed models of thiazolium salts and phosphonates with an electron withdrawing group to ensure the stability of possible unsymmetrical DTDAF [12e].

3H-thiazole-2-thiones **5** with one electron withdrawing group were prepared from ethyl 2-chloroacetylacetate or 3-chloroacetylacetone and dithiocarbamate salts and subsequently oxidized to thiazolium salts **4**, based on adopted literature methods [16] (Scheme 2). 3-phenyl-4,5-dimethoxycarbonyl-3H-thiazole-2-thione **5j** was prepared by the cycloaddition of 2-phenylimino-1,3-dithiolane with dimethyl acetylenedicarboxylate [12e]. Also we attempted to obtain 3-methyl-4,5-diethoxycarbonyl-1,3-thiazolium tetrafluoroborate **4b** in a very inefficient process of condensation of 3-chloro-2-oxo-butanedioic acid with thioformamide and following alkylation with trimethyloxonium tetrafluoroborate (Scheme 2).

SCHEME 2 Synthesis of dialkyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonates

The first experiments were performed by treating a solution of **4b** in acetonitrile with trimethyl phosphite in the presence of potassium iodide (Scheme 2). Even though we

observed the formation of the new compound, any attempts to isolate it failed, as the compounds decompose during chromatography. Next we tried to obtain (3-methyl-2,3-dihydro-benzothiazol-2-yl)-phosphonate **2a** from easily available N-methyl benzothiazolium iodide [19] and trimethyl phosphite; we also observed the formation of a new product, which decomposed during chromatography isolation.

It should be pointed out that Kucukbay [15] had prepared **2a** from bis(3-methylthiazolidyn-2-ylidene) [17].

We therefore repeated the experiment described in the literature [15] and compared this reaction mixture with the crude reaction mixture composed of N-methyl benzothiazolium iodide and trimethyl phosphite in the ^{31}P NMR experiment and observed a signal at 17,32 ppm which increase after addition of an authentic sample.

The failure of the first experiments and the fact that 1,3-dithio-2-yl phosphonates [4-7] and 1,3,4-thiadiazol-2-yl phosphonate [18] are stable and easily isolable led us to the supposition that the instability may be related to the higher electron donating properties of nitrogen.

In the next experiments we used a series of thiazolium salts with aryl on nitrogen atom and ethoxycarbonyl, or acetyl in the 5 position of the ring. Reactions of thiazolium salts with trimethyl phosphite in the presence of potassium iodide allowed us to produce the desired phosphonates, which were stable enough in in the cases of **2d-g** for chromatography purification under argon. However, we observed that any contact of sample with air, for example during preparation of NMR sample caused rapid decomposition of the purified product to a complicated mixture of compounds. As we could only measure ^{13}C and ^{1}H NMR spectra, our attempts to obtain good elemental analysis failed.

Surprisingly in the case of salt **4c** with acetyl group, the obtained phosphonate **2c** was not stable enough to isolate as a clean product. On the other hand, the instability of

phosphonate **2h** having the bulky 2-tert-butylphenyl group seems to confirm our supposition that electron donating properties of nitrogen have an influence on the stability of (2,3-dihydro-1,3-thiazol-2-yl)-phosphonates.

In order to increase the stability of the produced phosphonates, we tried to obtain a model with two electron withdrawing groups at positions 4 and 5. Unfortunately 3-phenyl-4,5-dimethoxycarbonyl-3H-thiazole-2-thione **5j** was completely resistant to oxidation and we were not able to prepare thiazolium salt in this manner. We also tried to introduce 3-nitrophenyl substitutent on a nitrogen atom to enhance the stability of the prepared phosphonate but the obtained thione **5i** was also resistant to oxidation to thiazolium salt.

As we indicate in our hypothesis, an alternative way to unsymmetrical DTDAF can led through (2,3-dihydro-1,3-thiazol-2-yl)-phosphonium salts. However, we observed that thiazolium salts do not react with triphenylphosphine. From the reaction mixtures of 3-methyl-4,5-diethoxycarbonyl-1,3-thiazolium tetrafluoroborate or 3-phenyl-4-methyl-5-ethoxycarbonyl-1,3-thiazolium hexafluorphosphate with triphenylphosphine in boiling acetonitrile after 3 hours we recovered quantitatively unreacted substrates (Scheme 2).

Despite the fact that only part of the prepared phosphonates showed moderate stability, we tried to perform Horner-Wadsworth-Emmons reactions between the prepared phosphonate and benzaldehyde as the simplest model. We treated freshly prepared and purified **2d** in the THF with tBuOK or LDA at -70°C following by addition of benzaldehyde. We obtained complex mixture of products; we therefore tried another experiment where we generated anion from **2d** at -70°C with LDA and after 0.5 hours quenched it with D_2O. Surprisingly we did not recover deutered starting material but instead again obtained a complex mixture of products. These results suggest that the antiaromatic anion of the phosphonate decomposes after generation, similar to the decomposition of 1,3-dithiol-2-yl-phophonate anion observed by Larsen [4].

EXPERIMENTAL

Reagents were purchased from Sigma-Aldrich. Acetonitrile was distilled from CaH_2 under argon. Analytical TLC was performed on aluminum sheets of silica gel UV-254 Merck. Flash chromatography was carried out using 40-63 microns silica gel Zeochem. The ^{1}H, ^{13}C and ^{31}P spectra were recorded at Varian Gemini 200 and Varian Unity Plus 500.

Commercially unavailable reagents were prepared by literature procedures as follows: bis(3-methylthiazolidyn-2-ylidene) [17], N-methyl benzothiazolium iodide **4a** [19], 2-phenylimino-1,3-dithiolane [20], 3-phenyl-4,5-dimethoxycarbonyl-1,3-thiazol-2(3H)-thion **5j** [12e].

4,5-diethoxycarbonyl-1,3-thiazol

To the cooled to -10°C suspension of diethyl oxalacetate sodium salt (10.5 g, 50 mmol) in dry ether (100 mL) was added SO_2Cl_2 (7.42 g, 55 mmol) over 0.5h. Then, the reaction was stirred 3h, filtered and solvent was removed under reduced pressure. The residue was dissolved in EtOH (100 mL) cooled to -10°C and suspension of $HC(S)NH_2$ in EtOH (100 mL) freshly prepared from $HC(O)NH_2$ (4.5 g, 100 mmol) and P_2S_5 (4.44 g, 20 mmol) was added dropwise. Reaction was stirred 24h at RT. EtOH was removed under reduced pressure, oil was dissolved in 100 mL of AcOEt and washed off with 1M NaOH (3x25 mL), dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2 as eluent.
Oily liquid. Yield: 1.61 g, 14%, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.86 (s, 1H), 4.47 (q, 2H, J = 7.32 Hz), 4.40 (q, 2H, J = 7.32 Hz), 1.43 (t, 3H, J = 7.32 Hz), 1.39 (t, 2H, J = 7.32 Hz).

3-methyl-4,5-diethoxycarbonyl-1,3-thiazolium tetrafluoroborate ***4b***

4,5-diethoxycarbonyl-1,3-thiazol (1.6 g, 7 mmol) was dissolved in CH_2Cl_2 and trimethyloxonium tetrafluoroborate (1.47 g, 10 mmol) was added. The solution was stirred 24h. Methanol (1mL) was added, solvents was removed under reduced pressure and the residue was crystallized from CH_2Cl_2/Et_2O.

White solid. Yield: 1.85 g, 79%, mp: 110-111 ºC, ^{1}H NMR (500 MHz, acetone-d_6) δ: 10.38 (s, 1H), 4.61 (q, 2H, *J* = 7.3 Hz), 4.51 (q, 2H, *J* = 6.8 Hz), 4.49 (s, 2H), 1.43 (m, 6H) ^{13}C NMR (125 MHz, acetone-d_6) δ: 164.0, 157.5, 157.1, 141.7, 134.2, 64.7, 64.2, 42.5, 13.5, 13.3.

General procedure for the preparation of 3H-thiazole-2-thiones ***5c-i***

3H-thiazole-2-thiones **5c-i** were obtained by the adopted method described in literature for analogous compounds [16]. To a solution of derivative of aniline (100 mmol) in DMSO (50 mL) was added 20 M NaOH (5 mL). The mixture was cooled to 0° C and CS_2 (100 mmol, 7.61 g, 6 mL) were added. The reaction was stirred for 1h at RT, cooled again to 0° C and ethyl 2-chloroacetylacetate (100 mmol, 16.45 g) or in the case of **5c** 3-chloroacetylacetone (100 mmol, 13.45 g) was added. The reaction mixture was stirred an additional 1h at RT, and ice (100 g) was added. The solidified product was filtered, suspended in EtOH (100 mL) treated with conc. HCl (5 mL) and heated to reflux for 1h. After cooling to RT the crude precipitated product was filtered and crystallized from EtOH.

3-phenyl-4-methyl-5-acetyl-3H-thiazole-2-thione ***5c***

Yellow solid. Yield: 13.44 g, 54%, mp: 171-174 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62-7.54 (m, 3H), 7.28- 7.23 (m, 2H), 2.43 (s, 3H), 2.33 (s, 3H) ^{13}C NMR (125 MHz, $CDCl_3$) δ: 189.7, 188.5, 147.6, 137.4, 130.5, 130.4, 128.4, 121.3, 30.6, 16.5.

3-phenyl-4-methyl-5-ethoxycarbonyl-3H-thiazole-2-thione ***5d***

White solid. Yield: 20.64 g, 74%, mp: 158-160 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.61-7.54 (m, 3H), 7.28- 7.23 (m, 2H), 4.34 (q, 2H, *J* = 7.3 Hz), 2.34 (s, 3H, Me), 1.37 (t, 3H, *J* = 7.3 Hz) ^{13}C NMR (125 MHz, $CDCl_3$) δ: 190.7, 160.4, 148.8, 137.6, 130.4, 130.3, 128.4, 112.6, 61.9, 15.8, 14.5.

3-(4-metylphenyl)-4-methyl-5-ethoxycarbonyl-3H-thiazole-2-thione ***5e***

White solid. Yield: 19.04 g, 65%, mp: 143-145 ºC, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.37 (d, 2H, *J* = 8.4 Hz), 7.10 (d, 2H, *J* = 8.4 Hz), 4.32 (q, 2H, *J* = 7.2 Hz), 2.44 (s, 3H), 2.32 (s, 3H), 1.36 (t, 3H, *J* = 7.2 Hz), ^{13}C NMR (125 MHz, $CDCl_3$) δ: 190.8, 160.4, 148.9, 140.6, 134.9, 131.1, 128.1, 112.5, 61.9, 21.7, 15.8, 14.5.

3-(4-bromophenyl)-4-methyl-5-ethoxycarbonyl-3H-thiazole-2-thione ***5f***

White solid. Yield: 22.19 g, 62%, mp: 145-148 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.72 (d, 2H, *J* = 8.3 Hz), 7.14 (d, 2H, *J* = 8.3 Hz), 4.33 (q, 2H, *J* = 6.8 Hz), 2.34 (s, 3H), 1.37 (t, 3H, *J* = 6.8 Hz), ^{13}C NMR (125 MHz, $CDCl_3$) δ: 190.2, 159.9, 147.9, 136.1, 133.4, 129.8, 124.3, 112.6, 61.6, 15.4, 14.2.

3-(4-chlorophenyl)-4-methyl-5-ethoxycarbonyl-3H-thiazole-2-thione ***5g***

White solid. Yield: 19.43 g, 62%, mp: 136-138 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.57 (d, 2H, *J* = 8.3 Hz), 7.20 (d, 2H, *J* = 8.3 Hz), 4.34 (q, 2H, *J* = 7.3 Hz), 2.34 (s, 3H), 1.37 (t, 3H, *J* = 7.3 Hz), ^{13}C NMR (125 MHz, $CDCl_3$) δ: 190.6, 160.2, 148.3, 136.5, 135.9, 130.8, 129.9, 112.9, 62.0, 15.8, 14.5.

3-(2-tert-butylphenyl)-4-methyl-5-ethoxycarbonyl-3H-thiazole-2-thione ***5h***

White solid. Yield: 8.71 g, 26%, mp: 107-109 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.70 (d, 1H, *J* = 8.3 Hz), 7.50 (t, 1H, *J* = 7.3 Hz), 7.36 (t, 1H, *J* = 7.3 Hz), 6.88 (d, 1H, *J* = 8.3 Hz), 4.33 (q, 2H, *J* = 7.3 Hz), 2.32 (s, 3H), 1.39 (t, 3H, *J* = 7.3 Hz), 1.30 (s, 9H), ^{13}C NMR (125 MHz, $CDCl_3$) δ: 191.2, 160.48, 149.6, 147.4, 134.4, 131.4, 130.5, 130.4, 128.0, 112.6, 61.9, 36.7, 32.0, 16.3, 14.5.

3-(3-nitrophenyl)-4-methyl-5-ethoxycarbonyl-3H-thiazole-2-thione ***5i***

White solid. Yield: 11.98 g, 37%, mp: 175-177 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.44 (dd, 1H, *J* = 8.3 Hz, *J* = 1.5 Hz), 8.17 (t, 1H, *J* = 1.5 Hz), 7.83 (t, 1H, *J* = 7.3 Hz), 7.64 (dd, 1H, *J* = 8.3 Hz, *J* = 1.5 Hz), 4.36 (q, 2H, *J* = 7.3 Hz), 2.38 (s, 3H), 1.39 (t, 3H, *J* = 7.3 Hz).

General procedure for the preparation of 1,3-thiazolium hexafluorophosphates ***4c-h***

1,3-thiazolium hexafluorophosphates **4c-h** were obtained by the adopted method described in literature for analogous compounds [16]. Compound **5c-h** (2 mmol) was dissolved in acetic acid (5 mL) and 30% H_2O_2 (0.67 mL) was added. The solution was stirred at RT for 1 h for **4c-e** or 2,5 h for **4f-g**. Acetic acid was removed under reduced pressure. To the oily residue 60% HPF_6 solution in water (0.29 mL) and water (20 mL) was added. Precipitate was filtered, washed with water, dissolved in CH_2Cl_2 and dried with $MgSO_4$. Solvent was removed under reduced pressure and the residue was crystallized from CH_2Cl_2/Et_2O.

3-phenyl-4-methyl-5-acetyl-1,3-thiazolium hexafluorophosphate ***4c***

White solid. Yield: 0.465 g, 64 %, mp: 87-90 ºC, ^{1}H NMR (500 MHz, acetone-d_6) δ: 10.49 (s, 1H), 7.85- 7.81 (m, 5H), 2.84 (s, 3H), 2.76 (s, 3H), ^{13}C NMR (125 MHz, acetone-d_6) δ= 189.3, 161.5, 150.6, 136.9, 136.7, 132.3, 130.7, 126.7, 29.7, 14.2.

3-phenyl-4-methyl-5-ethoxycarbonyl-1,3-thiazolium hexafluorophosphate ***4d***

White solid. Yield: 0.621 g, 79%, mp: 157-158 ºC, ^{1}H NMR (500 MHz, acetone-d_6) δ: 10.53 (s, 1H), 7.86- 7.79 (m, 5H), 4.55 (q, 2H, *J* = 7.3 Hz), 2.75 (s, 3H), 1.44 (t, 3H, *J* = 7.3 Hz), ^{13}C NMR (125 MHz, acetone-d_6) δ= 162.0 159.0, 152.9, 136.8, 132.4, 130.7, 127.5, 126.7, 63.6, 13.7, 13.6.

3-(4-metylphenyl)-4-methyl-5-ethoxycarbonyl-1,3-thiazolium hexafluorophosphate ***4e***

White solid. Yield: 0.651 g, 80%, mp: 130-132 ºC, ^{1}H NMR (200 MHz, acetone-d_6) δ: 9.63 (s, 1H), 7.45-7.38 (m, 4H), 4.46 (q, 2H, *J* = 7.2 Hz), 2.62 (s, 3H), 2.48 (s, 3H), 1.42 (t, 3H, *J* = 7.2 Hz) ^{13}C NMR (125 MHz, acetone-d_6) 160.1, 158.6, 152.2, 143.2, 133.6, 131.4, 127.9, 125.8, 63.8, 21.6, 14.3, 14.1.

3-(4-bromophenyl)-4-methyl-5-ethoxycarbonyl-1,3-thiazolium hexafluorophosphate ***4f***

White solid. Yield: 0.585 g, 62%, mp: 132-134 ºC, ^{1}H NMR (500 MHz, acetone-d_6) δ: 10.5 (s, 1H), 7.97 (dd, 2H, *J* = 9.1 Hz, *J* = 2.5 Hz), 7.80 (dd, 2H, *J* = 9.1 Hz, *J* = 2.5 Hz), 4.52 (q, 2H, *J* = 7.3 Hz), 2.75 (s, 3H), 1.42 (t, 3H, *J* = 7.3 Hz), ^{13}C NMR (125 MHz, acetone-d_6) δ: 162.2, 158.9, 152.9, 135.9, 133.8, 128.8, 127.5, 126.1, 63.6, 13.7, 13.6.

3-(4-chlorophenyl)-4-methyl-5-ethoxycarbonyl-1,3-thiazolium hexafluorophosphate ***4g***

White solid. Yield: 0.469 g, 55%, mp: 96-98 ºC, ^{1}H NMR (500 MHz, acetone-d_6) δ: 10.55 (s, 1H), 7.90 (dd, 2H, *J* = 8.8 Hz, *J* = 2.5 Hz), 7.85 (dd, 2H, *J* = 8.8 Hz, *J* = 2.5 Hz), 4.55 (q,

2H, *J* = 7.3 Hz), 2.78 (s, 3H), 1.45 (t, 3H, *J* = 7.3 Hz), ^{13}C NMR (125 MHz, acetone-d_6) δ: 162.4, 158.9, 152.9, 137.9, 135.4, 130.7, 128.7, 127.5, 63.6, 13.7, 13.6.

3-(2-tert-butylphenyl)-4-methyl-5-ethoxycarbonyl -1,3-thiazolium hexafluorophosphate ***4h***

White solid. Yield: 0.666 g, 74%, mp: 138-143 ºC, ^{1}H NMR (500 MHz, acetone-d_6) δ: 10.75 (s, 1H), 7.97 (d, 1H, *J* = 8.3 Hz), 7.77 (t, 1H, *J* = 8.3 Hz), 7.55 (m, 2H, *J* = 7.3 Hz), 4.55 (q, 2H, *J* = 7.3 Hz), 2.70 (s, 3H), 1.45 (t, 3H, *J* = 7.3 Hz), 1.26 (s, 9H), ^{13}C NMR (125 MHz, acetone-d_6) δ: 163.8, 159.5, 154.2, 146.4, 134.6, 133.2, 131.5, 129.9, 129.0, 128.8, 64.2, 36.9, 31.9, 14.7, 14.2.

General procedure for the preparation dimethyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonates ***2d-g***

To the solution of thiazolium salt **4d-g** in acetonitrile (20 mL) under argon, was added KI (0.5 mmol 83mg) and trimethyl phosphite(0.5mmol, 59μL). The reaction mixture was stirred and heated to reflux for 4 h. After removing solvent under reduced pressure, the residue was purified by flash chromatography. All operation must be done under argon atmosphere.

Dimethyl 3-phenyl-4-methyl-5-ethoxycarbonyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonate ***2d***

Eluent AcOEt/Hexane (3:1). Oil. Yield: 0.144 g, 80%, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40 (m, 2H), 7.28 (m, 3H), 5.48 (d, 1H, $^{2}J_{PH}$ = 5.8 Hz), 4.20 (q, 2H, J = 7.3 Hz), 3.78 (d, 3H, $^{3}J_{PH}$ = 2.9 Hz), 3.76 (d, 3H, $^{3}J_{PH}$ = 3.4 Hz), 2.09 (s, 3H), 1.30 (t, 3H, J = 7.3 Hz), ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.0, 151.7, 142.24 (d, $^{3}J_{PC}$ = 2.2 Hz), 129.8, 127.6, 127.3, 100.06 (d, $^{3}J_{PC}$

= 2.2 Hz), 65.6 (d, $^{1}J_{PC}$ = 178 Hz), 60.6, 54.5 (d, $^{2}J_{PC}$ = 6.8 Hz), 15.3, 14.6. ^{31}P NMR (200 MHz, $CDCl_3$) δ: 17.36.

Dimethyl 3-(4-metylphenyl)-4-methyl-5-ethoxycarbonyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonate ***2e***

Eluent AcOEt/Hexane (3:1). Oil. Yield: 0.139 g, 75%, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.20 (s, 4H), 5.47 (d, 1H, $^{2}J_{PH}$ = 6.3 Hz), 4.21 (q, 2H, J = 7.3 Hz), 3.78 (d, 3H, $^{3}J_{PH}$ = 4.8 Hz), 3.76 (d, 3H, $^{3}J_{PH}$ = 4.3 Hz), 2.37 (s, 3H), 2.09 (s, 3H), 1.30 (t, 3H, J = 7.3 Hz), ^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.7, 151.9, 139.12 (d, $^{3}J_{PC}$ = 1.5 Hz), 137.5, 130.0, 127.1, 98.5, 65.2 (d, $^{1}J_{PC}$ = 177 Hz), 60.1, 54.1 (d, $^{2}J_{PC}$ = 7.6 Hz), 20.9, 14.8, 14.3, ^{31}P NMR (200 MHz, $CDCl_3$) δ: 17.37.

Dimethyl 3-(4-bromophenyl)-4-methyl-5-ethoxycarbonyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonate ***2f***

Eluent AcOEt/Hexane (3:1). Oil. Yield: 0.168 g, 77%, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48 (d, 2H, J = 8.3 Hz), 7.17 (d, 2H, J = 8.3 Hz), 5.37 (d, 1H, $^{2}J_{PH}$ = 5.3 Hz), 4.19 (q, 2H, J = 7.3 Hz), 3.78 (d, 3H, $^{3}J_{PH}$ = 10.0 Hz), 3.76 (d, 3H, $^{3}J_{PH}$ = 10.0 Hz), 2.37 (s, 3H), 2.07 (s, 3H), 1.27 (t, 3H, J = 7.3 Hz), ^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.8, 150.6, 141.5 (d, $^{3}J_{PC}$ = 2.5 Hz), 132.9, 128.6, 121.0, 101.7, 65.51 (d, $^{1}J_{PC}$ = 179 Hz), 60.7, 54.7 (d, $^{2}J_{PC}$ = 7.1 Hz), 54.5 (d, $^{2}J_{PC}$ = 6.1 Hz), 15.2, 14.6, ^{31}P NMR (200 MHz, $CDCl_3$) δ: 17.11.

Dimethyl 3-(4-chlorophenyl)-4-methyl-5-ethoxycarbonyl (2,3-dihydro-1,3-thiazol-2-yl)-phosphonate ***2g***

Eluent AcOEt/Hexane (5:2). Oil. Yield: 0.137 g, 70%, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34 (d, 2H, J = 8.3 Hz), 7.23 (d, 2H, J = 8.3 Hz), 5.37 (d, 1H, $^{2}J_{PH}$ = 5.4 Hz), 4.18 (q, 2H, J = 7.1

Hz), 3.78 (d, 3H, $^{3}J_{PH}$ = 10.7 Hz), 3.76 (d, 3H, $^{3}J_{PH}$ = 10.2 Hz), 2.37 (s, 3H), 2.06 (s, 3H), 1.27 (t, 3H, J = 7.1 Hz), ^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.9, 150.8, 140.9, 133.2, 129.9, 128.4, 101.3, 65.55 (d, $^{1}J_{PC}$ = 179 Hz), 60.7, 54.7 (d, $^{2}J_{PC}$ = 7.6 Hz), 54.5 (d, $^{2}J_{PC}$ = 7.6 Hz), 15.2, 14.6, ^{31}P NMR (200 MHz, $CDCl_3$) δ: 17.13.

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