HETEROCYCLES, Vol. 90, No. 2, 2015, pp. 1205 - 1213. © 2015 The Japan Institute of Heterocyclic Chemistry
Received, 31st July, 2014, Accepted, 25th August, 2014, Published online, 5th September, 2014
DOI: 10.3987/COM-14-S(K)100

THIAZOLE/THIAZOLONE-FUSED CYCLOHEPTATRIENYL PHOSPHONATES: REACTIONS OF 2*H*-CYCLOHEPTA[*d*]THIAZOLE-2-THIONE AND -2-ONE WITH PHOSPHITES

Ohki Sato* and Ikumi Suzuki

Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo 255, Sakura-ku, Saitama 338-8570, Japan; E-mail: ohkisato@chem.saitama-u.ac.jp

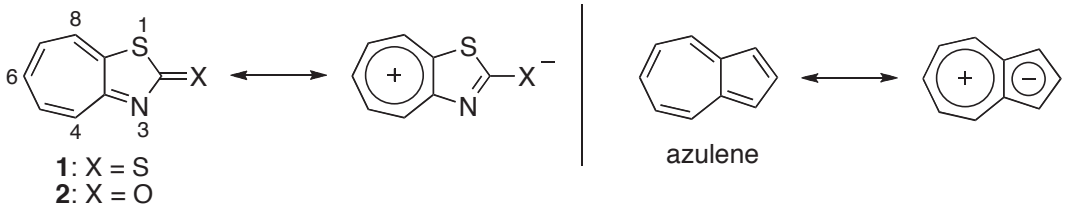
Abstract – 2*H*-Cyclohepta[*d*]thiazole-2-thione reacted with either trimethyl or dimethyl phosphite to furnish dimethyl 2-methylthio-4*H*-cyclohepta[*d*]thiazole-4-phosphonate and the regioisomers, 6- and 8-phosphonates. In the reaction with triphenyl phosphite, the successive *S*-methylation by methyl iodide and hydrolysis afforded an isomeric mixture of diphenyl 4-, 6- and 8-phosponates. Treatment of the oxygen analogue, 2*H*-cyclohepta[*d*]thiazol-2-one and triphenyl/diphenyl phosphite with/without hydrolysis gave diphenyl 3,4-dihydro-2*H*-cyclohepta[*d*]-thiazol-2-one-4-phosphonate and the isomeric 6- and 8-phosphonates.

INTRODUCTION

2*H*-Cyclohepta[*d*]thiazole-2-thione (**1**) and the oxygen analogue, -2-one (**2**), which have polarized structures similar to that of azulenes, are classified as non-benzenoid aromatics. Although some preparation methods[1-3] and reactions[3-5] of **1** and/or **2** had been reported, our previous work with dimethyl malonate/sodium hydride[3] was the only example in the reaction with nucleophiles. For further investigation of their reactivities, we focused on the reagents of phosphites. It is well known that trialkyl phosphites as a nucleophile are used in Michaelis-Arbuzov reaction[6-8] and Perkow reaction.[8,9] Reagents for Horner-Wadsworth-Emmons reaction[10] are prepared by the former reaction with alkyl halides. Trialkyl phosphites are also used to construct tetrathiafulvalene (TTF) derivatives by the condensation of trithio- and/or dithiocarbonates.[11] Therefore, whether phosphites act as a nucleophile or a condensation reagent toward **1** and **2** is of interest.

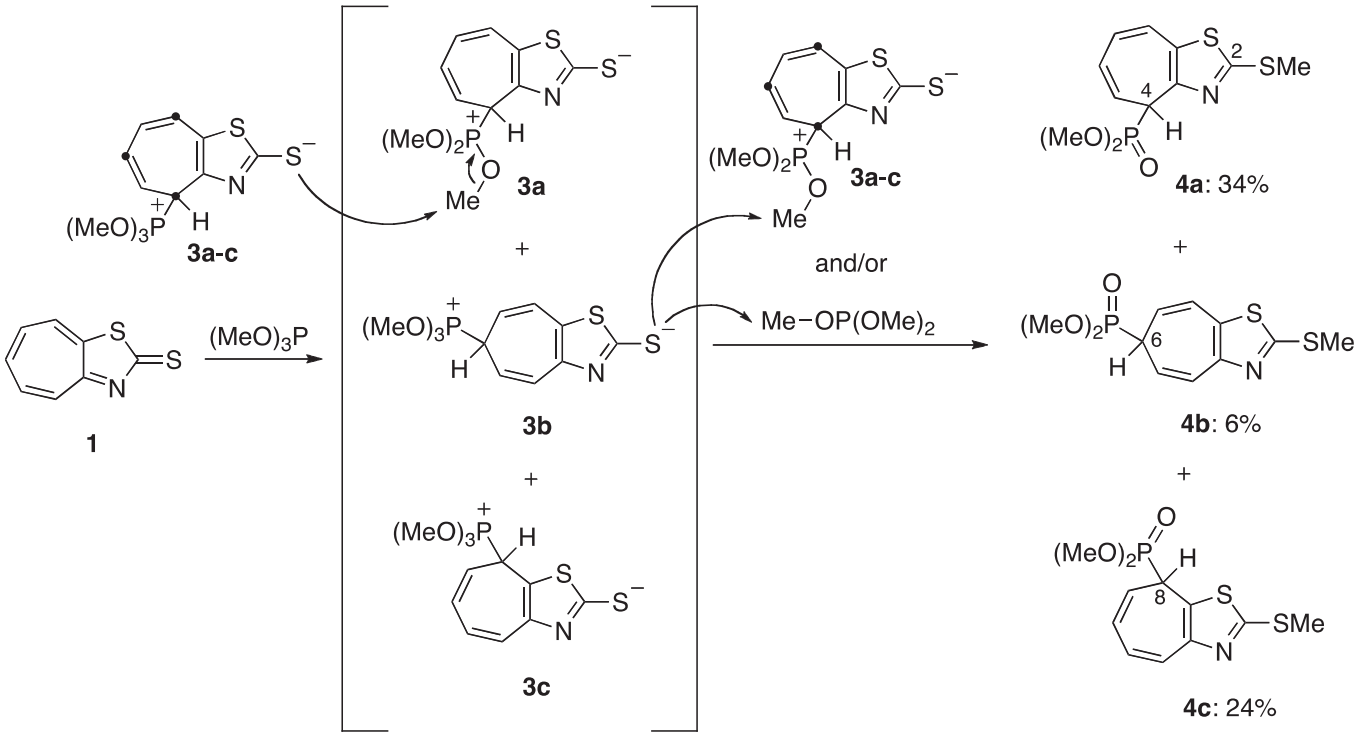
This paper is dedicated to Prof. Dr. Isao Kuwajima on the occasion of his 77th birthday.

In this manuscript, we report the reactions of **1** and **2** with several phosphites, which attack to a seven-membered ring moiety of the substrates as a nucleophile, producing three kinds of regioisomeric cycloheptatrienyl phosphonates fused with a thiazole/thiazolone ring.



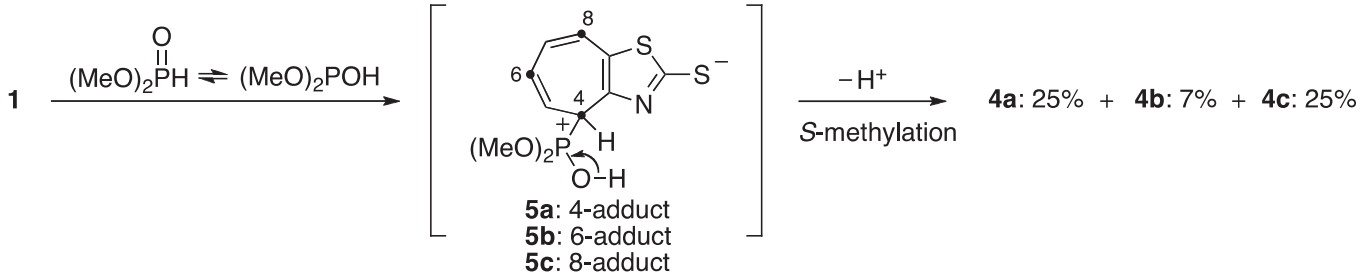
RESULTS AND DISCUSSION

The reaction of **1** and an excess amount of trimethyl phosphite without a solvent would generate an intermediate mixture of **3a**, **3b** and **3c**, phosphite-adducts at 4-, 6- and 8-positions of **1**, respectively (Scheme 1). The intermediates (**3a**-**c**) would be *S*-methylated by surplus trimethyl phosphite and/or the other molecules of **3a**-**c** acting as a trimethoxy phosphonium salt to form a 2-(methylthio)thiazole moiety, and would be also demethylated by the other molecules of **3a**-**c** acting as a thiolate to form a dimethyl phosphonate moiety. The final products were dimethyl 2-methylthio-4*H*-cyclohepta[*d*]thiazole-4-phosphonate (**4a**, 34%) and its 6- and 8-regioisomers (**4b** and **4c**, 6 and 24%). These products are classified both as cycloheptatrienyl phosphonates and thiazoles, and their chemical and physical properties attract much attention. Non-substituted dimethyl cycloheptatrienyl phosphonate had been synthesized by the reaction of tropylium tetrafluoroborate with sodium dimethyl phosphite.[12]



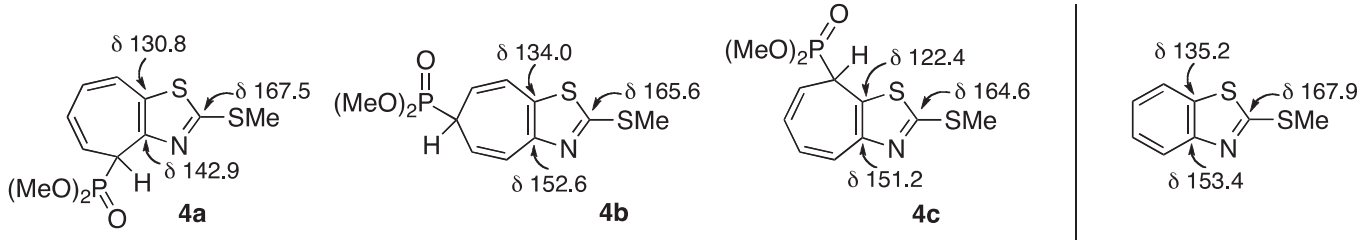
Scheme 1

Dimethyl phosphite has equilibrium between five-coordinated and three-coordinated structures. The intermediates (**5a**-**c**) are 4-, 6- and 8-adducts of **1** with the three-coordinated one (Scheme 2), and a phosphonate moiety would be formed smoothly by the deprotonation instead of demethylation as mentioned in Scheme 1. Indeed, treatment with dimethyl phosphite afforded the same products (**4a**-**c**) as described above in 25, 7 and 25% yields, respectively. In this case, *S*-methylation of the intermediates would be caused by surplus dimethyl phosphite.



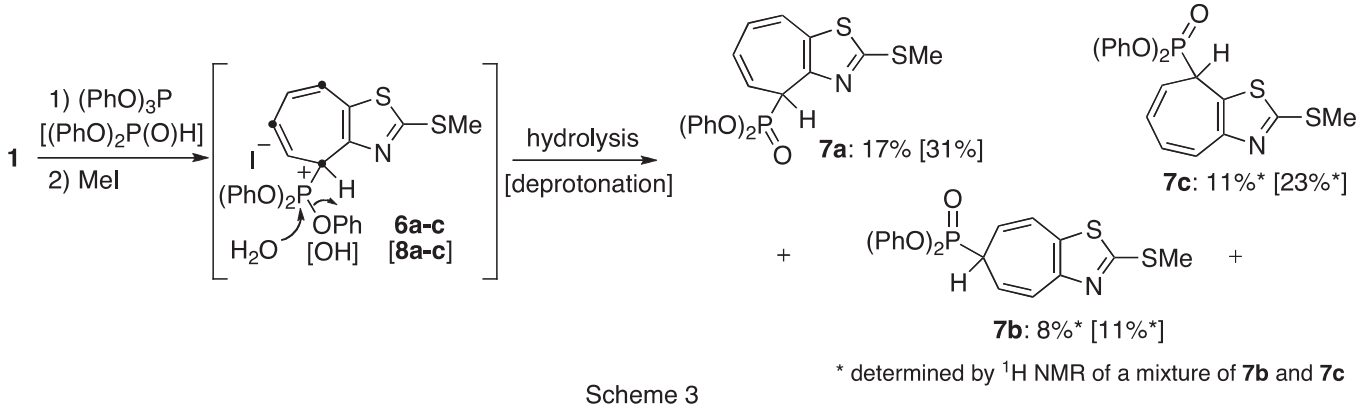
Scheme 2

Prepared dimethyl phosphonates (**4a**-**c**) were all yellowish brown oil. The H-H and C-H relationship was determined by their H-H COSY and HMQC NMR spectra. From these results, the peaks of their quaternary carbons were revealed. As shown in the following figure, C-2 peaks of **4a**-**c** were assigned at δ 167.5, 165.6 and 164.6, respectively, by comparison with the peak of 2-(methylthio)benzothiazole (δ 167.9).[13] These results indicate that **4a**-**c** have a *S*-methyl thiazole framework instead of a *N*-methyl thiazole-2-thione one. In the same way, peaks of C-3a and C-8a were assigned at δ 142.9, 130.8 (for **4a**), 152.6, 134.0 (for **4b**) and 151.2, 122.4 (for **4c**) by comparison with corresponding peaks of the benzothiazole (δ 153.4, 135.2).[13] The longest-wavelength peaks in the UV-VIS absorption spectra of **4a**-**c** appeared at 331, 306 and 296 nm, respectively, on the basis of each expanded π-conjugated system. That is, 4-phosphonate (**4a**) has longer conjugated one than that of 6- and 8-isomers (**4b** and **4c**). ^{31}P NMR, IR and MS spectra of **4a**-**c** were also consistent with their proposed structures, respectively.



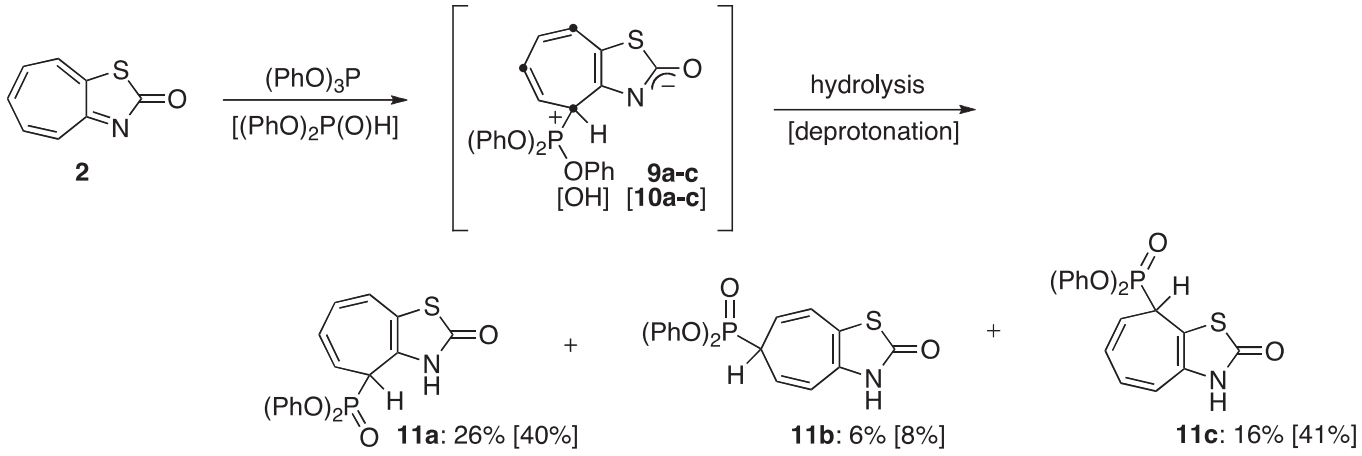
The reaction of **1** with triphenyl phosphite and the successive *S*-methylation by methyl iodide would generate 2-methylthio-4-, 6- and 8-phosphite-adducts (**6a**-**c**, Scheme 3), which were hydrolyzed to furnish diphenyl 4-phosphonate (**7a**, 17%) and an inseparable mixture of 6- and 8-phosphonates (**7b** and **7c**, 8 and 11%). In the case with diphenyl phosphite as shown by square brackets in Scheme 3, the same products (**7a**, **7b** and **7c**, 31, 11 and 23%) were obtained by formal deprotonation of the intermediates (**8a**-**c**). The deprotonation process might occur before the *S*-methylation one by methyl iodide. Isolated

compound (**7a**) was yellow oil, and its ^{1}H, ^{13}C and ^{31}P NMR and MS spectra were consistent with the proposed structure. In the case of **7b** and **7c**, their structures were presumed by comparison with ^{1}H NMR spectra of dimethyl 6- and 8-phosphonates (**4b** and **4c**). That is, the coupling pattern at a seven-membered ring moiety of **7b** and **7c** was very close to that of **4b** and **4c**, respectively. The reaction of **1** and triphenyl/diphenyl phosphite without methyl iodide gave a complex mixture.



Scheme 3

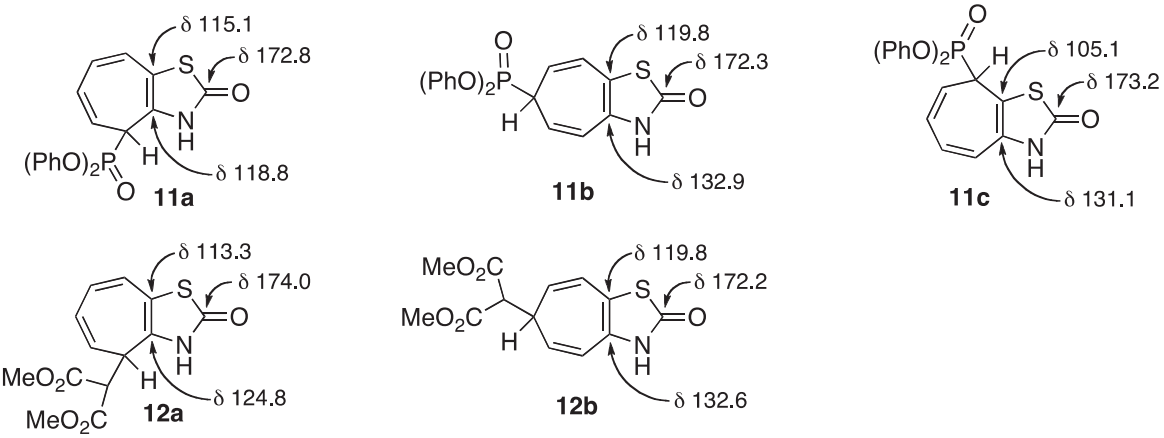
2*H*-Cyclohepta[*d*]thiazol-2-one (**2**), the oxygen analogue of **1**, reacted with trimethyl or dimethyl phosphite to give a complex mixture, and no product could be determined in either case. Treatment of **2** with triphenyl or diphenyl phosphite would form corresponding intermediates (**9a**-**c**) or (**10a**-**c**), which were hydrolyzed or deprotonated to afford diphenyl 3,4-dihydro-2*H*-cyclohepta[*d*]thiazol-2-one-4-phosphornate (**11a**: colorless needles) and the regioisomeric 6- and 8-phosphonates (**11b**: yellow oil and **11c**: colorless powder). Those yields were 26, 6 and 16% with triphenyl phosphite or 40, 8 and 41% with diphenyl phosphite, respectively (Scheme 4). In the case of the reaction with methyl iodide, *N*- and/or *O*-methylation of **9**/**10** did not occurred, and the same products (**11a**-**c**) as described above were confirmed in the reaction mixture.



Scheme 4

The H-H and C-H relationship was determined by their H-H COSY and HMQC NMR spectra. As shown in the following figure, C-2 peaks of **11a**-**c** were assigned at δ 172.8, 172.3 and 173.2, respectively, as a carbonyl carbon by comparison with the peaks of 4- and 6-adducts of malonate [**12a** (δ 174.0) and **12b** (δ

172.2)] derived from **2** with dimethyl malonate/sodium hydride.[3] The 8-regioisomer of malonate-adduct had not been formed by the reaction. In the same way, peaks of C-3a and C-8a were assigned at δ 118.8, 115.1 (for **11a**), 132.9, 119.8 (for **11b**) and 131.1, 105.1 (for **11c**) by comparison with the peaks of **12a** (δ 124.8, 113.3) and **12b** (δ 132.6, 119.8).[3] The NOE correlation appeared between NH and H-4 of 4-phosphonate (**11a**). Other data such as ^{31}P NMR, IR, UV-VIS and MS spectra and elemental analysis results (for **11a** and **11c**) also supported proposed structures of **11a**-**c**.



In conclusion, we have succeeded in the preparation of thiazole/thiazolone-fused cycloheptatrienyl phosphonates (**4a**-**c**, **7a**-**c** and **11a**-**c**) by the reactions of 2*H*-cyclohepta[*d*]thiazole-2-thione (**1**) and -2-one (**2**) with several phosphites. Further work, aimed at Horner-Wadsworth-Emmons reaction[10] of the prepared phosphonates with carbonyl compounds for construction of various thiazole/thiazolone-fused heptafulvenes, is in progress.

EXPERIMENTAL

Mps were determined with a Laboratory Devices MEL-TEMP apparatus and are uncorrected. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained with Bruker AV500, AV400 and/or AV300 spectrometers. IR spectra were obtained with a Perkin Elmer System 2000 FT instrument and electronic spectra (UV-VIS) with a JASCO V-560 spectrophotometer. MS spectra were obtained with a Bruker AutoflexIII spectrometer. Unless otherwise stated the spectra were taken in the following solvents/media: IR, neat and/or KBr; UV-VIS, MeOH and/or CH_2Cl_2; ^{1}H, ^{13}C and ^{31}P NMR, $CDCl_3$ and/or MeOH-d_4; MS spectra were taken at a MALDI-TOF method. The progress of reactions was followed by TLC method using Merck Silica gel $60F_{254}$.

The reaction of 2*H*-cyclohepta[*d*]thiazole-2-thione (1) with trimethyl phosphite: A mixture of **1** (50 mg, 2.8 x 10^{-1} mmol) and trimethyl phosphite (15 mol *eq*.) was heated without a solvent at 100-110 °C for 3 h under Ar. THF (0.5 mL) and H_2O (0.5 mL) were added to the reaction mixture, and the solution was heated at 50 °C for 3 h to hydrolyze surplus trimethyl phosphite. The resulting mixture was extracted with sat. *aq*. $NaHCO_3$/CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent was removed under

reduced pressure to give a crude mixture of **4a**, **4b** and **4c**. The mixture was purified by SiO_2 column chromatography and HPLC (SiO_2, EtOAc/EtOH) to give **4a** (29 mg, 34%), **4b** (5.3 mg, 6%) and **4c** (20 mg, 24%).

Dimethyl 4-phosphonate (4a): yellowish brown oil; ^{1}H NMR ($CDCl_3$) δ 2.66 (s, 3H), 3.68 (d, J = 10.5 Hz, 3H), 3.75 (d, J = 10.5 Hz, 3H), 4.38 (dd, J = 25.8, 8.3 Hz, 1H), 5.54 (ddd, J = 10.7, 9.0, 8.3 Hz, 1H), 6.21 (ddd, J = 10.7, 6.3, 4.5 Hz, 1H), 6.30 (dd, J = 11.3, 6.3 Hz, 1H), 6.63 (d, J = 11.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 16.7, 41.9 (d, J = 144.6 Hz), 53.2 (d, J = 7.5 Hz), 53.4 (d, J = 6.3 Hz), 120.8, 121.0 (d, J = 7.5 Hz), 127.0, 129.1 (d, J = 10.1 Hz), 130.8 (d, J = 7.5 Hz), 142.9 (d, J = 6.3 Hz), 167.5; ^{31}P NMR ($CDCl_3$) δ 27.95; IR (neat) ν 1248, 1035, 831; UV-VIS (MeOH, log ε) λ_{max} 264 (3.64), 331 (3.91); MS (MALDI-TOF, dithranol): m/z 302 ([M-H]$^+$), 303 (M$^+$), 304 ([M+H]$^+$); HRMS (MALDI-TOF, dithranol) Calcd for $C_{11}H_{13}NO_3PS_2$: 302.0075. Found: 302.0079.

Dimethyl 6-phosphonate (4b): yellowish brown oil; ^{1}H NMR ($CDCl_3$) δ 2.63 (dtt, J = 20.5, 6.5, 1.0 Hz, 1H), 2.71 (s, 3H), 3.79 (d, J = 10.5 Hz, 3H), 3.81 (d, J = 10.5 Hz, 3H), 5.51 (ddd, J = 12.5, 9.5, 6.5 Hz, 1H), 5.61 (ddd, J = 12.5, 9.5, 6.5 Hz, 1H), 6.77 (dt, J = 9.5, 1.0 Hz, 1H), 6.95 (dt, J = 9.5, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 16.4, 36.7 (d, J = 152.2 Hz), 53.1 (d, J = 6.3 Hz, 2C), 116.8 (d, J = 3.8 Hz), 118.5 (d, J = 5.0 Hz), 121.7 (d, J = 16.3 Hz), 126.4 (d, J = 16.3 Hz), 134.0, 152.6, 165.6; ^{31}P NMR ($CDCl_3$) δ 32.79; IR (neat) ν 1256, 1030, 827; UV-VIS (MeOH, log ε) λ_{max} 233 (4.07), 252 (3.85), 306 (3.72); MS (MALDI-TOF, dithranol): m/z 302 ([M-H]$^+$), 303 (M$^+$), 304 ([M+H]$^+$); HRMS (MALDI-TOF, dithranol) Calcd for $C_{11}H_{13}NO_3PS_2$: 302.0075. Found: 302.0086.

Dimethyl 8-phosphonate (4c): yellowish brown oil; ^{1}H NMR ($CDCl_3$) δ 2.67 (s, 3H), 3.75 (d, J = 10.5 Hz, 3H), 3.76 (d, J = 10.5 Hz, 3H), 3.93 (dd, J = 25.8, 8.1 Hz, 1H), 5.50 (ddd, J = 10.0, 8.5, 8.1 Hz, 1H), 6.18 (ddd, J = 10.0, 6.3, 3.3 Hz, 1H), 6.37 (dd, J = 11.6, 6.3 Hz, 1H), 6.99 (d, J = 11.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 16.5, 36.5 (d, J = 150.9 Hz), 53.4 (d, J = 6.3 Hz), 53.5 (d, J = 7.5 Hz), 120.2 (d, J = 6.3 Hz), 122.4 (d, J = 7.5 Hz), 127.1, 127.7, 129.3 (d, J = 11.3 Hz), 151.2 (d, J = 10.1 Hz), 164.6 (d, J = 2.5 Hz); ^{31}P NMR ($CDCl_3$) δ 27.51; IR (neat) ν 1252, 1029, 826; UV-VIS (MeOH, log ε) λ_{max} 267 (4.03), 296 (3.62); MS (MALDI-TOF, dithranol): m/z 302 ([M-H]$^+$), 303 (M$^+$), 304 ([M+H]$^+$); HRMS (MALDI-TOF, dithranol) Calcd for $C_{11}H_{13}NO_3PS_2$: 302.0075. Found: 302.0094.

The reaction of 1 with dimethyl phosphite: A mixture of **1** (152 mg, 8.5 x 10^{-1} mmol) and dimethyl phosphite (20 mol *eq*.) was heated without a solvent at 100-110 °C for 3 h under Ar. THF (1.5 mL) and H_2O (1.5 mL) were added to the reaction mixture, and the solution was heated at 50 °C for 3 h to hydrolyze surplus dimethyl phosphite. The resulting mixture was extracted with sat. *aq*. $NaHCO_3/CH_2Cl_2$. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a crude mixture of **4a**, **4b** and **4c**. The mixture was purified by SiO_2 column chromatography and HPLC (SiO_2, EtOAc/EtOH) to give **4a** (65 mg, 25%), **4b** (18 mg, 7%) and **4c** (65 mg, 25%).

The reaction of 1 with triphenyl or diphenyl phosphite: A mixture of **1** and triphenyl or diphenyl phosphite (6.1 or 9.3 mol *eq*.) was heated without a solvent at 100-110 °C for 3 h under Ar. Methyl iodide (10 mol *eq*.) was added at room temperature, and the mixture was stirred for 2 h to form methylthio ethers. THF (1.5 mL) and H_2O (1.5 mL) were added to the reaction mixture, and the solution was heated at 50 °C for 3 h to hydrolyze surplus triphenyl/diphenyl phosphite and triphenoxy phosphonium salts (in the only case with triphenyl phosphite). The resulting mixture was extracted with sat. *aq*. $NaHCO_3$/CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a crude mixture of **7a**, **7b** and **7c**. The mixture was purified by SiO_2 column chromatography and HPLC (SiO_2, EtOAc/EtOH) to give **7a** (17 or 31%) and an inseparable mixture of **7b** (8 or 11%) and **7c** (11 or 23%). The yields of **7b** and **7c** were determined by ^{1}H NMR spectra of their mixture.

Diphenyl 4-phosphonate (7a): yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.61 (s, 3H), 4.75 (dd, J = 22.5, 8.5 Hz, 1H), 5.66 (dt, J = 11.5, 8.5 Hz, 1H), 6.29-6.33 (m, 2H), 6.63 (d, J = 11.5 Hz, 1H), 7.05 (d like, J = 8.0 Hz, 2H), 7.10 (t like, J = 8.0 Hz, 1H), 7.15 (t like, J = 8.0 Hz, 1H), 7.19 (d like, J = 8.0 Hz, 2H), 7.25 (t like, J = 8.0 Hz, 2H), 7.30 (t like, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 16.4, 42.7 (d, J = 147.1 Hz), 120.0 (d, J = 7.5 Hz), 120.3 (d, J = 3.8 Hz, 2C), 120.7 (d, J = 5.0 Hz, 2C), 121.0, 124.8, 125.0, 127.2 (d, J = 1.3 Hz), 129.5 (2C), 129.6 (2C), 129.8 (d, J = 11.3 Hz), 131.5 (d, J = 7.5 Hz), 141.7 (d, J = 6.3 Hz), 150.5 (d, J = 10.0 Hz, 2C), 167.5; ^{31}P NMR ($CDCl_3$) δ 14.99; MS (MALDI-TOF, dithranol): *m/z* 426 ([M-H]$^+$), 427 (M$^+$), 428 ([M+H]$^+$); HRMS (MALDI-TOF, dithranol) Calcd for $C_{21}H_{17}NO_3PS_2$: 426.0388. Found: 426.0398.

An inseparable mixture of diphenyl 6- and 8-phosphonates (7b and 7c): Selected ^{1}H NMR ($CDCl_3$) of **7b** δ 2.71 (s, 3H), 2.94 (dtt, J = 21.0, 6.5, 1.5 Hz, 1H), 5.68 (ddd, J = 13.0, 9.5, 6.5 Hz, 1H), 5.80 (ddd, J = 13.0, 9.5, 6.5 Hz, 1H), 6.83 (dt, J = 9.5, 1.5 Hz, 1H), 7.03 (dt, J = 9.5, 1.5 Hz, 1H), 7.16-7.20 (m, 6H), 7.29-7.33 (m, 4H); Selected ^{31}P NMR ($CDCl_3$) of **7b** δ 20.37; Selected ^{1}H NMR ($CDCl_3$) of **7c** δ 2.67 (s, 3H), 4.26 (dd, J = 25.5, 8.0 Hz, 1H), 5.65 (ddd, J = 10.5, 8.5, 8.0 Hz, 1H), 6.28 (ddd, J = 10.5, 6.5, 3.5 Hz, 1H), 6.38 (dd, J = 11.5, 6.5 Hz, 1H), 7.01 (d, J = 11.5 Hz, 1H), 7.09-7.11 (m, 4H), 7.13-7.17 (m, 2H), 7.27-7.31 (m, 4H); Selected ^{31}P NMR ($CDCl_3$) of **7c** δ 14.86.

The reaction of 2*H*-cyclohepta[*d*]thiazol-2-one (2) with triphenyl or diphenyl phosphite: A mixture of **2** and triphenyl or diphenyl phosphite (6.2 or 8.4 mol *eq*.) was heated without a solvent at 100-110 °C for 3 h under Ar. THF (1.5 mL) and H_2O (1.5 mL) were added to the reaction mixture, and the solution was heated at 50 °C for 3 h to hydrolyze surplus triphenyl/diphenyl phosphite and triphenoxy phosphonium salts (in the only case with triphenyl phosphite). The resulting mixture was extracted with sat. *aq*. $NaHCO_3$/ CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a mixture of crude **11a**, **11b** and **11c**. The mixture was purified by SiO_2 column

chromatography and HPLC (SiO_2, EtOAc/EtOH) to give **11a** (26 or 40%), **11b** (6 or 8%) and **11c** (16 or 41%), respectively.

Diphenyl 4-phosphonate (11a): colorless needles; mp 192-193 °C (dec.); ^{1}H NMR ($CDCl_3$) δ 4.15 (dd, J = 25.5, 8.5 Hz, 1H), 5.45 (dt, J = 10.5, 8.5 Hz, 1H), 6.22-6.27 (m, 2H), 6.30-6.34 (m, 1H), 7.05-7.08 (m, 4H), 7.15 (t like, J = 7.5 Hz, 2H), 7.27-7.30 (m, 4H), 9.62 (brs, 1H); ^{1}H NMR (MeOH-d_4) δ 4.62 (dd, J = 26.5, 8.5 Hz, 1H), 5.54 (ddd, J = 11.5, 8.5, 8.0 Hz, 1H), 6.23 (dd, J = 11.5, 6.5 Hz, 1H), 6.28 (d, J = 11.5 Hz, 1H), 6.38 (dt, J = 11.0, 6.5 Hz, 1H), 7.02 (d like, J = 7.5 Hz, 2H), 7.07 (d like, J = 7.5 Hz, 2H), 7.17-7.22 (m, 2H), 7.32 (t like, J = 7.5 Hz, 2H), 7.34 (t like, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 39.5 (d, J = 150.9 Hz), 115.1 (d, J = 11.3 Hz), 116.5 (d, J = 6.3 Hz), 118.8 (d, J = 6.3 Hz), 120.27 (d, J = 5.0 Hz, 2C), 120.33 (d, J = 3.8 Hz, 2C), 123.6, 125.5, 125.6, 126.7, 129.87 (2C), 129.89 (2C), 130.5 (d, J = 6.3 Hz), 150.0 (d, J = 7.5 Hz), 150.1 (d, J = 10.1 Hz), 172.8; ^{31}P NMR ($CDCl_3$) δ 13.34; IR (KBr) ν 3157, 1670, 1487, 1249, 1211, 1185, 1162, 949, 765; UV-VIS (MeOH, log ε) λ_{max} 336 (3.51); UV-VIS (CH_2Cl_2, log ε) λ_{max} 329 (3.52); MS (MALDI-TOF, dithranol): m/z 396 ([M-H]$^+$), 397 (M$^+$), 398 ([M+H]$^+$). Anal. Calcd for $C_{20}H_{16}NO_4PS$: C, 60.45; H, 4.06. Found: C, 60.38; H, 3.98.

Diphenyl 6-phosphonate (11b): yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.84 (dt, J = 20.5, 6.5 Hz, 1H), 5.53 (ddd, J = 13.3, 9.5, 6.5 Hz, 1H), 5.66 (ddd, J = 13.3, 9.5, 6.5 Hz, 1H), 6.45 (dd, J = 9.5, 1.0 Hz, 1H), 6.51 (dd, J = 9.5, 1.0 Hz, 1H), 7.17-7.20 (m, 6H), 7.32 (t like, J = 8.0 Hz, 4H), 9.91 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ 38.0 (d, J = 155.9 Hz), 113.6 (d, J = 3.8 Hz), 117.5 (d, J = 3.8 Hz), 119.6 (d, J = 17.6 Hz), 119.8, 120.49 (d, J = 2.5 Hz, 2C), 120.53 (d, J = 2.5 Hz, 2C), 123.1 (d, J = 17.6 Hz), 125.5 (2C), 129.9 (4C), 132.9, 150.06 (d, J = 7.5 Hz), 150.12 (d, J = 7.5 Hz), 172.3; ^{31}P NMR ($CDCl_3$) δ 19.95; IR (neat) ν 3168, 1685, 1488, 1263, 1186, 1162, 942, 765; UV-VIS (MeOH, log ε) λ_{max} 261 (3.62), 268 (3.60), 303 (3.51); UV-VIS (CH_2Cl_2, log ε) λ_{max} 262 (3.76), 269 (3.73), 310 (3.52); MS (MALDI-TOF, dithranol): m/z 396 ([M-H]$^+$), 397 (M$^+$), 398 ([M+H]$^+$); HRMS (MALDI-TOF, dithranol) Calcd for $C_{20}H_{15}NO_4PS$: 396.0459. Found: 396.0461.

Diphenyl 8-phosphonate (11c): colorless powder; mp 67 °C (dec.); ^{1}H NMR ($CDCl_3$) δ 4.05 (dd, J = 26.0, 9.0 Hz, 1H), 5.63 (dt, J = 10.5, 9.0 Hz, 1H), 6.24-6.31 (m, 3H), 7.08 (d like, J = 8.5 Hz, 2H), 7.11-7.17 (m, 4H), 7.25-7.31 (m, 4H), 10.10 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ 38.6 (d, J = 152.2 Hz), 105.1 (d, J = 6.3 Hz), 119.6 (d, J = 6.3 Hz), 120.3 (d, J = 5.0 Hz, 2C), 120.4 (d, J = 5.0 Hz, 2C), 120.8, 125.25, 125.32, 129.72 (2C), 129.75 (d, J = 7.5 Hz), 129.78 (2C), 130.1, 131.1 (d, J = 10.1 Hz), 150.15 (d, J = 8.8 Hz), 150.23 (d, J = 8.8 Hz), 173.2; ^{31}P NMR ($CDCl_3$) δ 14.44; IR (KBr) ν 3136, 1666, 1488, 1263, 1211, 1188, 1160, 929, 768; UV-VIS (MeOH, log ε) λ_{max} 324 (3.35); UV-VIS (CH_2Cl_2, log ε) λ_{max} 330 (3.37); MS (MALDI-TOF, dithranol): m/z 396 ([M-H]$^+$), 397 (M$^+$), 398 ([M+H]$^+$). Anal. Calcd for $C_{20}H_{16}NO_4PS$: C, 60.45; H, 4.06. Found: C, 60.24; H, 3.88.

REFERENCES

1. T. Nozoe, S. Ito, K. Kitahara, and T. Ozeki, *Tohoku Daigaku Hisuiyoeki Kagaku Kenkyusho Hokoku,* 1961, **10**, 251 (*Chem. Abstr.*, 1961, **55**, 25917e).
2. Y. Mitsumoto and M. Nitta, *Heterocycles*, 2001, **55**, 2131.
3. O. Sato, N. Ando, and T. Toma, *Heterocycles*, 2014, **88**, 1573.
4. N. Abe, T. Nishiwaki, and M. Shigematsu, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2881.
5. K. Saito, N. Ito, and S. Ando, *Heterocycles*, 2002, **56**, 59.
6. A. Michaelis and R. Kaehne, *Ber.*, 1898, **31**, 1048.
7. A. E. Arbuzov, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 687.
8. B. A. Arbuzov, *Pure Appl. Chem.*, 1964, **9**, 307.
9. W. Perkow, *Ber.*, 1954, **87**, 755.
10. W. S. Wadsworth, Jr., *Org. React.*, 1977, **25**, 73; and cited references in this review.
11. M. Bendikov, F. Wudl, and D. F. Perepichka, *Chem. Rev.*, 2004, **104**, 4891; and cited references in this review.
12. D. G. Gilheany, N. T. Thompson, and B. J. Walker, *Tetrahedron Lett.*, 1987, **28**, 3843.
13. SDBSweb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, February, 2013).