Synthesis and Synthetic Application of Phosphonoketene Dithioacetals. New Synthesis of Dithioallenes and (α-Dithiocarboxyvinyl)phosphonates

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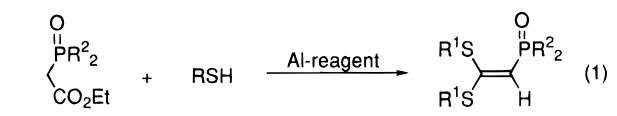
Phosphonoketene dithioacetals **3a**−**e** were obtained in good yields by the reaction of ethyl phosphonoacetates **1a**,**b** with 2−4 equiv of thiols **2a**−**c** in the presence of an alkylaluminum dichloride or dialkylaluminum chlorides. Reaction of 2,2-dithio-1-phosphonovinyl anions with aldehydes afforded allylic alcohols **4**−**7**, **11**−**18** in good to moderate yields. Treatment of the alcohols **4**−**6** with *t*-BuOK in THF led to symmetrical [2 + 2] cycloadducts **20**−**22** of 1,1-(ethylenedithio)-allenes in moderate yields, while a similar reaction of the alcohols **11**−**13** produced a mixture of symmetrical and unsymmetrical [2 + 2] cycloadducts of 1,1-(trimethylenedithio)allenes, **23a**−**25a** and **23b**−**25b**, in 55−94% yields. The alcohol **15** on a similar treatment gave 3-*tert*-butyl-1,1-bis-(ethylthio)allene (**26**) in quantitative yield. The structures of **20** and **23b** were determined by X-ray analysis. Treatment of the alcohols **15** and **18** with trifluoromethanesulfonic acid/*n*-Bu_4NX (X = Br, I) or triphenylphosphine/CBr_4 in CH_2Cl_2 afforded α-phosphonodithioacryclic acid esters **34** and **35** in 25−52% yields. The tandem Michael−Wittig reaction of **35** with sodium salt of 2-pyrrole-carbaldehyde in DMF gave ethyl 3-phenyl-3*H*-cyclopenta[*a*]pyrrole-2-dithiocarboxylate (**36**) in 25% yield.

Development of ketene dithioacetals containing various functional groups and their synthetic applications have been widely studied.[1] Phosphonoketene dithioacetals are expected to be versatile reagents in organic synthesis, since they are anticipated to act as ketene dithioacetals and/or as vinylphosphonates.[2] To our knowledge, studies on their synthesis and synthetic utilization have been limited .[3] As a continuation of our studies on vinylphosphonates, we became interested in the synthesis of novel phosphonoketene dithioacetals and related compounds. We now report a convenient synthesis of phosphonoketene dithioacetals and their application to the synthesis of dithioallenes *via* the Horner−Emmons−Wittig reaction.[4] We also describe the synthesis of a new type of vinylphosphonate bearing a dithioester group at the α-position from the phosphonoketene dithioacetals.

Results and Discussion

Synthesis of Phosphonoketene Dithioacetals. Phosphonoketene dithioacetals having no substituent at the α-position to phosphorus should be widely utilized as starting compounds in organic synthesis, since various functional groups could be introduced at the α-position. First, we attempted to prepare the phosphonoketene dithioacetals according to the Corey procedure.[5] Treatment of triethyl phosphonoacetate (**1a**) with thiols and trimethyl- or triethylaluminum failed to give the expected phosphonoketene dithioacetals (eq 1) (entries 1 and 2 in Table 1). This result can be explained by the deprotonation of **1a**, due to the strong basicity of dialkylaluminum sulfide. Next, we used diethyl- or dimethylaluminum chloride or ethylaluminum dichloride in order to lower the basicity of the aluminum reagent. The reaction of triethyl phosphonoacetate (**1a**) with thiols **2a**−**c** proceeded in the presence of diethyl- or dimethylaluminum chloride or ethylaluminum dichloride to produce the expected diethylphosphonoketene dithioacetals **3a**−**c** in good yields (entries 4−10). A similar treatment of ethyl diphenylphosphinylacetate (**1b**) with organoaluminum chlorides also led to the corresponding ketene dithioacetals **3d** and **3e** in excellent yields (entries 11 and 12). In comparison with the conventional synthetic method *via* addition of the carbanions of active methylene compounds to carbon disulfide followed by alkylation,[3a] our method using dialkylaluminum chlorides has advantages with regard to yield, simplicity of manipulation, and wide applicability to the synthesis of phosphonoketene dithioacetals unsubstituted at the α-position to phosphorus.



1a: R^2 = OEt
1b: R^2 = Ph

2a: R = $(CH_2)_3SH$
2b: R = $(CH_2)_2SH$
2c: R = Et

3a: R^1 R^1 = $(CH_2)_3$; R^2 = OEt
3b: R^1 R^1 = $(CH_2)_2$; R^2 = OEt
3c: R^1 = Et; R^2 = OEt
3d: R^1 R^1 = $(CH_2)_3$; R^2 = Ph
3e: R^1 R^1 = $(CH_2)_2$; R^2 = Ph

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(1) For reviews of ketene dithioacetals, see: (a) Kolb, M. *Synthesis* **1990**, 71. (b) Junjappa, H.; Ila, H.; Asokan, C. V. *Tetrahedron* **1990**, *46*, 5423.

(2) For a review of vinylphosphonates, see: Minami, T.; Motoyoshiya, J. *Synthesis* **1992**, 333.

(3) For the synthesis of diphenylphosphorylketene and phosphonoketene dithioacetals, see: (a) Schaumann, E.; Grabley, F. F. *Liebigs Ann. Chem.* **1979**, 1715. (b) Schaumann, E.; Fittkau, S. *Bull. Soc. Chim. Belg.* **1985**, *94*, 462. (c) Schaumann, E.; Fittkau, S. *Synthesis* **1983**, 449.

(4) For the Wittig reaction of [bis(alkylthio)vinylidene]triphenyl phosphoranes with a reactive carbonyl reagent, diphenylketene, see: Bestmann, H. J.; Roth, K. *Tetrahedron Lett.* **1981**, *22*, 1681.

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Table 1. Synthesis of Phosphonoketene Dithioacetals[a]

entry	starting material 1	starting material 2[b]	Al-reagent	molar ratio of Al-reagent/1	reaction condition temp/°C	reaction condition time/h	product[d] (yield/%)
1	**1a**	**2a**	Et_3Al	2.0	−78 to rt	12	**3a** (0)
2	**1a**	**2a**	Me_3Al	2.0	−78 to rt	12	**3a** (0)
3	**1a**	**2a**	Me_2AlCl	2.0	−78 to rt	12	**3a** (16)
4	**1a**	**2a**	Me_2AlCl	4.0	−78 to rt	4	**3a** (71)
5	**1a**	**2a**	Et_2AlCl	2.0	−78 to −20	10	**3a** (59)
6	**1a**	**2a**	Et_2AlCl	3.0	−78 to rt	4	**3a** (66)
7	**1a**	**2a**	Et_2AlCl	4.0	−78 to rt	4	**3a** (82)
8	**1a**	**2a**	Et_2AlCl	4.0	−78 to rt	4	**3a** (64)
9	**1a**	**2b**	Et_2AlCl	4.0	rt	4	**3b** (83)
10	**1a**	**2c**[c]	Et_2AlCl	4.0	rt	12	**3c** (69)
11	**1b**	**2a**	Et_2AlCl	3.3	−78 to rt	4	**3d** (93)
12	**1b**	**2b**	Et_2AlCl	4.0	rt	4	**3e** (97)

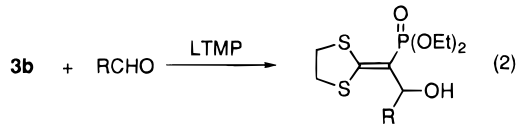
[a] All reactions were carried out in CH_2Cl_2, unless otherwise noted. [b] Molar ratio of **2a** or **2b**/Al-reagent is 0.5. [c] Molar ratio of **2c**/Al-reagent is 1.0. [d] Isolated yield.

Table 2. Synthesis of Diethyl [1-(1,3-Dithiolan-2-ylidene)-2-hydroxyethyl]phosphonates 4−7 from 3b and Aldehyde

entry	RCHO	reaction condition[a] temp/°C	reaction condition[a] time/h	product[b] (yield/%)
1	R = *t*-Bu	−78 °C	0.8	**4** (76)
2	R = *i*-Pr	−78 °C	0.8	**5** (73)
3	R = c-Hex	−78 °C	2	**6** (74)
4	R = Ph	−78 °C	0.8	**7** (76)

[a] All reactions were carried out in THF. [b] Isolated yield.

Reactions of Phosphonoketene Dithioacetals. Although various α-hetero-substituted vinyl anions have been widely utilized as extremely important intermediates in organic synthesis,[6] only an α-phosphonoallenyl lithium[7] has been known as an α-phosphonovinyl anion. We then explored the generation of the carbanions and their reaction with aldehydes. Five-membered cyclic dithioacetal **3b** was treated with lithium 2,2,6,6-tetramethylpiperidide (LTMP) in THF at −78 °C for 1 h, and following addition of aldehydes, the expected allylic alcohols **4**−**7** were produced in high yields (eq 2) (Table 2). In contrast to **3b**, a similar treatment of six-membered cyclic dithioacetal **3a** resulted in a complex

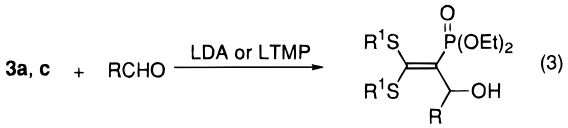


4: R = *t*-Bu **6**: R = *c*-Hex
5: R = *i*-Pr **7**: R = Ph

mixture. In order to test whether or not the α-phosphonovinyl anion of **3a** is formed under the above conditions, the treatment of **3a** with LTMP followed by quenching with aqueous ammonium chloride was performed, leading to a ring-expanded product, diethyl 6,7-dihydro-5*H*-1,4-dithiepin-2-ylphosphonate (**10a**) in 50% yield (Scheme 1). Another six-membered cyclic ketene dithioacetal **3d** and an acyclic ketene dithioacetal **3c** also underwent a similar rearrangement to give the corresponding products **10d** and **10c**, respectively, while five-membered cyclic ketene dithioacetal **3b** was recovered after the same treatment.[8]

These results show that 2,2-(trimethylenedithio)- or 2,2-diethythio-1-phosphonovinyl anions **8** would undergo facile elimination of a thiolate anion to give reactive thioethynylphosphonates **9a**, **9c** or a thioethynylphosphine oxide **9d**, and they are subjected to a subsequent nucleophilic attack of the thiolate anion to produce the 1,2-migration products of the thio group, **10a**,**c**,**d**.

An alternative approach was tried to trap the 2,2-dithio-1-phosphonovinyl anions with aldehydes before the elimination of the thiolate anion. Addition of a mixture of dithiovinylphosphonates **3a** or **3c** and the desired aldehydes to a solution of LTMP in THF at −78 °C successfully produced the desired allylic alcohols **11**−**18** in good to moderate yields (eq 3) (Table 3). These are the first examples of reactions of 2,2-dithio-1-phosphonovinyl anions.



11–18

11: R = *t*-Bu; R^1 R^1 = $(CH_2)_3$ **15**: R = *t*-Bu; R^1 = Et
12: R = *i*-Pr; R^1 R^1 = $(CH_2)_3$ **16**: R = *i*-Pr; R^1 = Et
13: R = *c*-Hex; R^1 R^1 = $(CH_2)_3$ **17**: R = *c*-Hex; R^1 = Et
14: R = Ph; R^1 R^1 = $(CH_2)_3$ **18**: R = Ph; R^1 = Et

Our next efforts were directed at the synthesis of dithioallenes from the allylic alcohols through elimination of a phosphate moiety.[4,9] Treatment of the 1,3-dithiolane-containing allylic alcohol **4** with *t*-BuOK in THF at room temperature for 12 h did not give an expected 3-*tert*-butyl-1,1-(ethylenedithio)allene, but a product **20**, which proved to a dimer of the allene by mass spectral data (*m*/*z* 375), in 29% yield (entries 1 in Table 4) (Scheme 2).[10] The ^1H and ^{13}C NMR spectra of the dimer **20**

(5) For the synthesis of ketene dithioacetals using dithiol−trimethylaluminum, see: Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 5829.

(6) For preparation of α-hetero (B, Si, S, Se)-substituted vinylcarbanions and their synthetic application, see: For R_2B (a) Pelter, A.; Smith, K.; Jones, K. D. *J. Chem. Soc., Perkin Trans 1*, **1992**, 747. For R_3Si (b) Grobel, B.-Th.; Seebach, D. *Chem. Ber.* **1977**, *110*, 867. For RS, see ref 7b. (c) Takeda, T.; Furukawa, H.; Fujimori, M.; Suzuki, K.; Fujiwara, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1863. For RSe, see ref 7b. For a review of synthesis and synthetic application of α-seleno and α-telluro vinylcarbanions, see: (d) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 410.

(7) Macomber, R. S.; Hemling, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 343.

(8) There is no unambiguous proof that **3a** opens to **9b**.

(9) For the synthesis of 1,1-(dialkylthio)-1,2-propadienes, see: (a) Clinet, J. C.; Julia, S. *J. Chem. Res. (M)* **1978**, 1714. (b) Saalfrank, R. W. *Isr. J. Chem.* **1985**, *26*, 181.

(10) For the cyclodimerization of allenes, see: Pasto, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 37.

Scheme 1

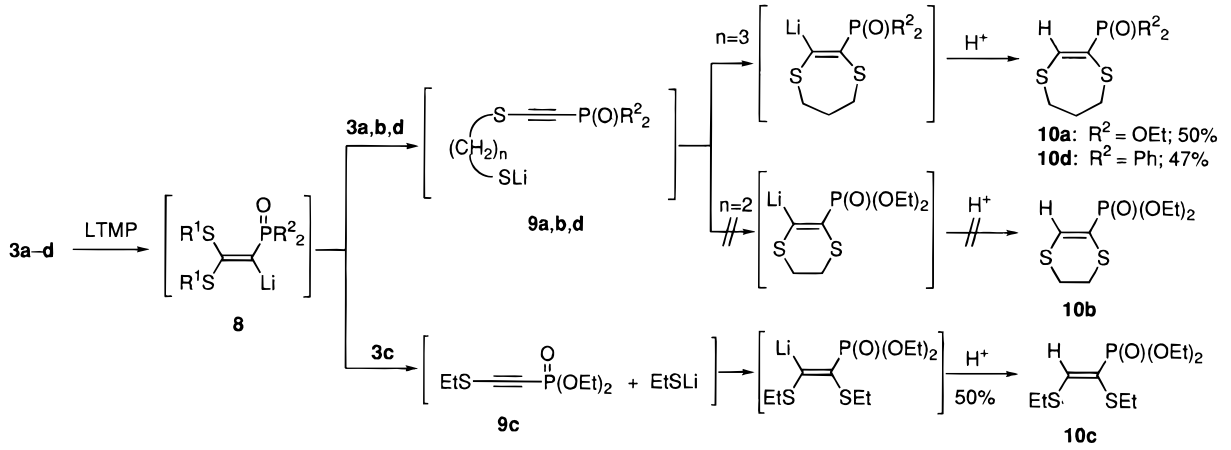


Table 3. Synthesis of Diethyl [1-Bis[(alkylthio)methylene]-2-hydroxyethyl]phosphonates 11-18 from 3a,c and Aldehyde

	starting material		reaction condition[a]		product[b]
entry	**3**	RCHO	temp/°C	time/h	(yield/%)
1	**3a**	R = *t*-Bu	−78	1.5	**11** (87)
2		R = *i*-Pr	−78	1.5	**12** (86)
3		R = c-Hex	−78	1.5	**13** (90)
4		R = Ph	−78	1.5	**14** (83)
5	**3c**	R = *t*-Bu	−78	1.5	**15** (64)
6		R = *i*-Pr	−78	2	**16** (22)
7		R = c-Hex	−78	1.5	**17** (30)
8		R = Ph	−78	1.5	**18** (53)

[a] All reactions were carried out in THF. [b] Isolated yield.

showed *tert*-butyl methyl protons (18H) at δ 1.25 and olefinic protons (2H) at δ 5.63 as a singlet each, and six signals at δ 30.9, 33.6, 40.1, 82.5, 131.8 (sp^2-carbon), and 138.6 (sp^2-carbon), suggesting a symmetrical dimer. The ^1H and ^{13}C NMR spectral data for **20** did not provide enough information for a detailed structural assignment. Therefore, X-ray crystallography was employed to establish the exact structure **20**. The structure of **20** was successfully determined to be a symmetrical head-to-head [2 + 2] cycloadduct, (11*Z*,12*Z*)-11,12-dineopentylidene-1,4,7,10-tetrathiodispiro[4.0.4.2]dodecane (Figure 1).[11] Moreover, allylic alcohols **5** and **6** also underwent dimerization under similar conditions to produce symmetrical [2 + 2] cycloadducts **21** and **22** in moderate to low yields (entries 2 and 3 in Table 4).

In contrast, treatment of the allylic alcohols **11**−**13** containing the 1,3-dithiane ring with *t*-BuOK in THF at room temperature for 4−6 h afforded a mixture of both head-to-head and head-to-tail dimers of the dithioallenes, **23a**−**25a** and **23b**−**25b**, in 55−94% yields (entries 4−6 in Table 4).

The ^1H NMR spectrum of **23a** showed characteristic peaks of *tert*-butyl methyl protons (s, 18H), and olefinic protons (s, 2H) at δ 1.31 and 5.73, respectively, while that of **23b** exhibited two magnetically nonequivalent *tert*-butyl methyl protons as two singlets at δ 1.12 (9H) and 1.32 (9H), a methine proton (s, 1H) at δ 3.05, and an olefinic proton (s, 1H) at δ 5.91. Furthermore, the ^{13}C

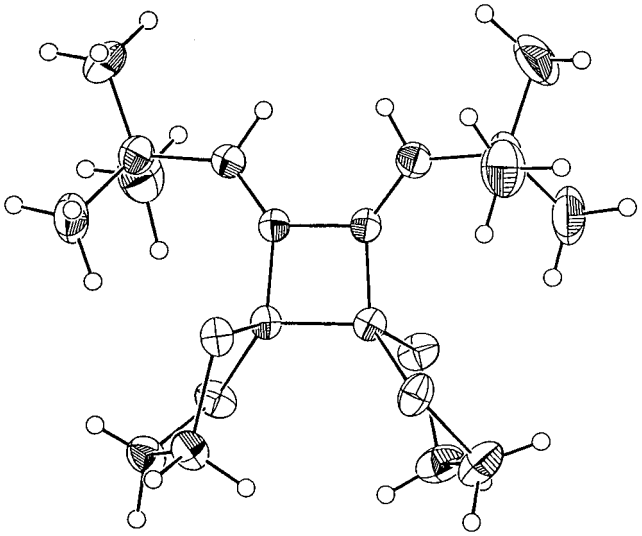


Figure 1. ORTEP diagram of the X-ray structure of **20**. 30% probabilities.

NMR spectrum of **23a** showed seven signals at δ 23.7, 29.7, 31.7, 33.1, 69.7, 133.4 (sp^2-carbon), and 138.3 (sp^2-carbon), whereas that of **23b** displayed sixteen signals including four olefinic signals at δ 122.4, 138.5, 140.6, and 142.1 (Table 5). On the basis of the similarity in the NMR spectra between **20** and **23a**, the adduct **23a** is determined to be a symmetrical [2 + 2] dimerization product of 3-*tert*-butyl-1,1-(trimethylenedithio)allene. The structure of **23b** was also unambiguously determined by X-ray analysis to be an unsymmetrical [2 + 2] cycloadduct, (*Z*)-3-*tert*-butyl-2-(1,3-dithian-2-ylidene)-1-neopentylidene-5,9-dithiospiro[3.5]nonane (Figure 2).[12]

As shown in Scheme 2, these results indicate that the symmetrical dimerization products **20**−**22** and **23a**−**25a** arised from [2 + 2] cycloaddition of the dithioallenes at the terminal C1−C1 carbons and at the internal C2−C2 carbons, while the unsymmetrical adducts **23b**−**25b** were formed *via* the cycloaddition at the terminal C1−C3 carbons and at the internal C2−C2 carbons.On the other

(11) X-ray crystallographic analysis of **20**. $C_{18}H_{28}S_4$, M = 372.66, orthorhombic, space group $P2_12_12_1$ (#19), a = 11.2484(9), b = 18.9460(9), c = 9.678(1) Å, V = 2062.5(2) Å^3, Z = 4, D_{calc} = 1.200 g cm^{-3}, graphite monochromated radiation λ(Cu Kα) = 1.54178 Å, μ = 41.70 cm^{-1}, T = 20.0 °C. Data collected on a Rigaku AFC7R diffractometer. Structure solved by direct methods. Final agreement statistics are: R = 0.030, R_w = 0.039.

(12) X-ray crystallographic analysis of **23b**. $C_{20}H_{32}S_4$, M = 400.71, triclinic, space group $P\bar{1}$ (#2), a = 9.08(2), b = 22.362(5), c = 21.226(4) Å, α = 90.0000, β = 90.01(5), γ = 90.0000°, V = 4311(7) Å^3, Z = 10, D_{calc} = 6.173 g cm^{-3}, graphite monochromated radiation λ(Mo Kα) = 0.71069 Å, μ = 22.05 cm^{-1}, T = 20.0 °C. Data collected on a Rigaku AFC7R diffractometer. Structure solved by direct methods. Final agreement statistics are R = 0.029, R_w = 0.033. The authors have deposited the atomic coordinates for the structures of **20** and **23b** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

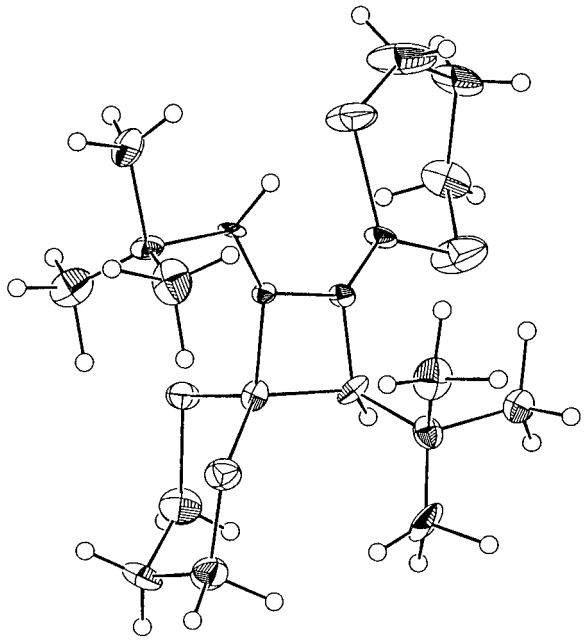


Figure 2. ORTEP diagram of the X-ray structure of **23b**. 30% probabilities.

Scheme 2

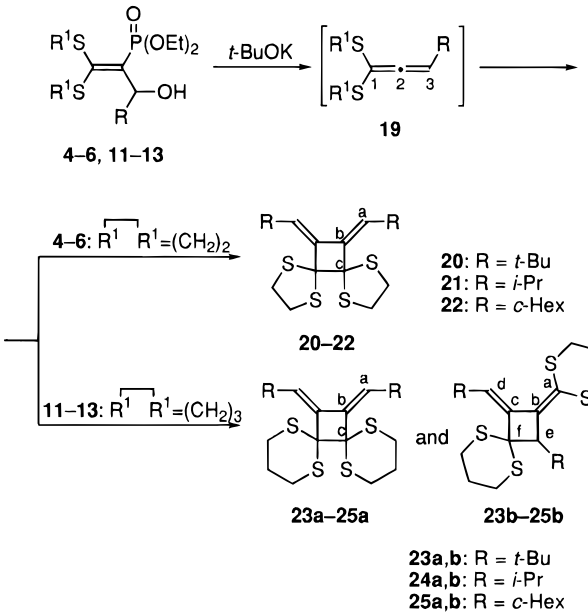


Table 4. [2 + 2] Cycloadducts of Dithioallenes

entry	starting material	reaction[a] time/h	product[b] (yield/%)	product ratio[c] sym:unsym
1	**4**	12	**20** (29)	100:0
2	**5**	12	**21** (52)	100:0
3	**6**	12	**22** (23)	100:0
4	**11**	6	**23a**+**23b** (94)[d]	37:63
5	**12**	6	**24a**+**24b** (55)[d]	77:23
6	**13**	4	**25a**+**25b** (69)[d]	71:29

[a] All reactions were carried out in the presence of *t*-BuOK (1.1 equiv) in THF at room temperature. [b] Isolated yield. [c] Ratios of symmetrical dimer to unsymmetrical dimer were determined by ^{1}H NMR analysis. [d] Total yield of symmetrical and unsymmetrical dimers.

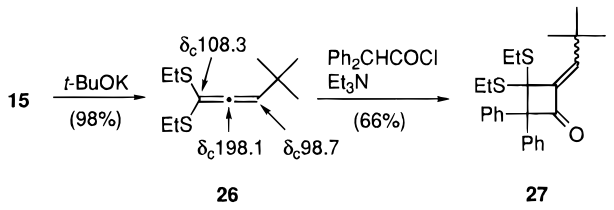
hand, treatment of a bis(ethylthio)-substituted allylic alcohol **15** under similar conditions gave 3-*tert*-butyl-1,1-di(ethylthio)allene (**26**) as a comparatively stable product in quantitative yield (Scheme 3).[13,14] These results

Table 5. ^{13}C NMR Data[a] of [2 + 2] Cycloadducts 20-25

compd	^{13}C chemical shifts,[b] ppm C-a	C-b	C-c	C-d	C-e	C-f
20	131.8	138.6	82.5			
21	131.1	137.3	81.2			
22	129.6	138.1	81.0			
23a	133.4	138.3	69.7			
23b	142.1	140.6	138.5	122.4	56.4	69.0
24a	131.8	138.2	69.4			
24b	138.7	137.3	136.3	122.8	56.4	64.3
25a	130.3	138.9	69.3			
25b	139.4	137.0	135.8	122.0	56.6	64.1

[a] See Scheme 2 for carbon labeling. [b] Chemical shifts for $CDCl_3$ solutions with respect to Me_4Si.

Scheme 3



demonstrate that, in contrast to the acyclic dithioallene, the cyclic dithioallenes are very susceptible to dimerization even under mild conditions. The reaction of dithioallene **26** with excess diphenylketene, generated *in situ* from diphenylacetyl chloride and triethylamine in benzene at room temperature, gave exclusively 3,3-bis(ethylthio)-2-neopentylidene-4,4-diphenylcyclobutanone (**27**) in 62% yield.[15]

To gain insight into the difference of the reactivities of dithioallenes, PM3 calculations on allenes **28**, **29**, **30** and their dimers **31a**,**b**, **32a**,**b** were performed with MOPAC Ver. 6.01.[16] Our calculations show the following: (i) The orbital energy gap $E_{\pi-\mathrm{LUMO}} - E_{\pi-\mathrm{HOMO}}$ of the allene **30** is greater than those of **28**, **29** (Table 6); (ii) The total energy of the unsymmetrical dimers are lower than those of the symmetrical dimers (Table 7). The calculation result (i) can explain the fact that ethylenedithio and trimethylenedithioallene are more susceptible to dimerization than bis(ethylthio)allene. As shown in Table 4, the less stable symmetrical dimers of dithioallenes were predominantly obtained except for entry 4. These experimental facts indicate that the direction of the dimerization is not thermodynamically controlled.

Synthesis and Synthetic Application of Ethyl α-(Diethylphosphono)dithioacrylate. As shown above, α-(hydroxymethyl)phosphonoketene dithioacetals were readily obtained. When **15** was exposed to hydrolytic cleavage using trifluoromethanesulfonic acid (1.0 equiv) in CH_2Cl_2 at room temperature, *S*-ethyl [(*Z*)-2-(*tert*-butyl)-1-diethylphosphono]thioacrylate (**33**) was exclusively ob-

(13) Purification of the dithioallene **26** on silica gel was difficult due to the ease of hydrolysis.

(14) Dithio allenes are labile and difficult to be isolated; e.g., 1,1-bis(methylthio)-3,3-dimethyl-1,2-propadiene, which is prepared by the reaction of 1-lithio-3-chloro-3-methyl-1-butyne and dimethyl disulfide, is isomerized on silica gel into 1,1-bis(methylthio)-3-methyl-1,3-butadiene, see ref 9a.

(15) For the [2 + 2] cycloaddition reaction between ketene and allene, see: (a) Bertrand, M.; Maurin, R.; Gras, J. L.; Gil, G. *Tetrahedron* **1975**, *31*, 849. (b) Bertrand, M.; Gras, J. L.; Gore, J. *Tetrahedron* **1975**, *31*, 857. For *ab initio* studies on the mechanism of the cycloaddition between ketene and allene, see: (c) Fang, D. C.; Fu, X. Y. *Int. J. Quant. Chem.* **1994**, *50*, 93.

(16) MOPAC Ver. 6, Stewart, J. J. P. *QCPE Bull.* **1989**, *9*, 10. Revised as Ver. 6.01 by Hirano, T., University of Tokyo, for HITAC and UNIX machines, *JCPE Newsletter* **1980**, *1*, 10.

Table 6. PM3 Calculated π-HOMO/π-LUMO Gaps of the Dithioallenes 28, 29, and 30

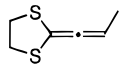
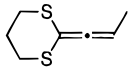
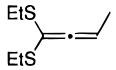
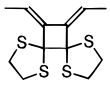
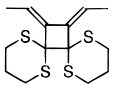
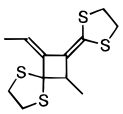
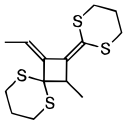
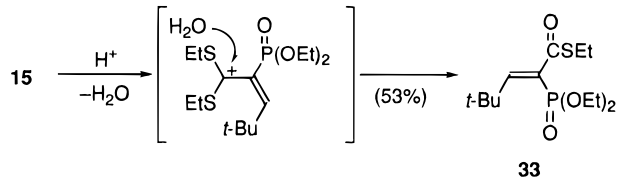
compounds	π–HOMO (eV)	π–LUMO (eV)	gap (eV)
 **28**	–8.689	–0.345	8.344
 **29**	–8.682	–0.343	8.339
 **30**	–8.656	–0.112	8.544

Table 7. PM3 Calculated Total Energies of the Dimers of Dithioallenes 28 and 29

dimers	Total energy (eV)	dimers	Total energy (eV)
 **31a**	–2410.9	 **32a**	–2709.9
 **31b**	–2411.6	 **32b**	–2710.5

Scheme 4



33

tained in 53% yield (Scheme 4). The stereochemistry of **33** was determined to be (*Z*)-configuration on the basis of the phosphorus−*trans*-vinyl proton NMR coupling constant of $^3J_{P-H} = 48.2$ Hz.[17]

This reaction probably proceeded *via* a mechanism which included attack of water on an allylic carbocation stabilized by two sulfur atoms. This mechanism prompted us to synthesize a new class of compounds, α-(phosphono)dithioacrylic acid esters, from α-(hydroxymethyl)-phosphonoketene dithioacetals by conducting the reaction in the presence of a nucleophile appropriate for attack on the alkyl carbon adjacent to sulfur. Although the chemistry of dithiocarboxylic acid esters (RCS_2R') has been well studied, their novel homologues, α-phosphonodithioacrylic acid esters are unknown to our knowledge.[18] They are expected to act as extremely useful dithio-functionalized two-carbon homologation reagents.

Treatment of the α-(hydroxymethyl)phosphonoketene dithioacetals with a strong acid was tried in the presence of halogen anion as a nucleophile (method A). The dithioacetals **15** or **18** were treated with trifluoromethanesulfonic acid (1.0 equiv) and tetrabutylammonium halides (X = I or Br) (10 equiv) in CH_2Cl_2 at room temperature

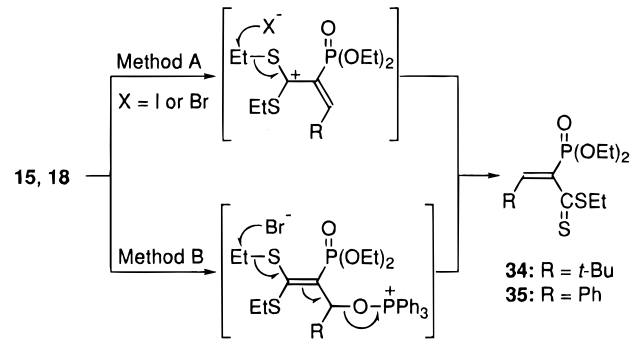
(17) Minami, T.; Utsunomiya, T.; Nakamura, S.; Okubo, M.; Kitamura, N.; Okada, Y.; Ichikawa, J. *J. Org. Chem.* **1994**, *59*, 6717.

Table 8. Synthesis of α-Phosphonodithioacrylates

entry	method	starting material	reaction time/h	product[a] (yield/%)
1	A[b]	**15**	21	**34** (52)
2	A[c]	**15**	16	**34** (31)
3	A[b]	**18**	41	**35** (25)
4	B	**15**	61	**34** (31)
5	B	**18**	61	**35** (45)

[a] Isolated yield. [b] *n*-Bu_4NI was used. [c] *n*-Bu_4NBr was used.

Scheme 5



for 16−41 h, and the desired α-phosphonodithioacrylic acid esters **34** or **35** with the *(E)*-configuration were obtained in 25−52% yields as orange liquids (entries 1−3 in Table 8) (Scheme 5). This transformation was also performed under neutral conditions using phosphonium salts (method B). On treatment of **15** or **18** with triphenylphosphine (1.2 equiv)−CBr_4 (2.0 equiv) in CH_2Cl_2 at room temperature, (*E*)-**34** or (*E*)-**35** were similarly obtained in 31% or 45% yields, respectively (entries 4 and 5 in Table 8). In contrast to the vinylphosphonate **33**, the NMR spectra of these vinylphosphonates (*E*)-**34** and (*E*)-**35** exhibited the phosphorus−*cis*-vinyl proton coupling constant $^3J_{P-H} = 26.6$ and 24.1 Hz, respectively (see Experimental Section).[17]

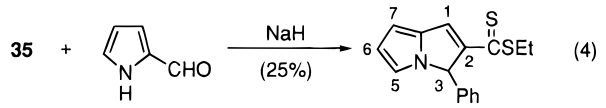
In order to examine the ability of α-phosphonodithioacrylic acid esters to act as reagents for dithio-functionalized two-carbon homologation, we attempted to synthesize 3*H*-cyclopenta[*a*]pyrrole-2-dithiocarboxylate from the α-phosphonodithioacrylate and 2-pyrrolecarbaldehyde,[19] since functionalized 3*H*-pyrrolizine systems are not readily accessible and have been shown to have useful biological properties.[20] Ethyl α-(diethylphosphono)-*β*-phenyldithioacrylate (**35**) was treated with the sodium salt of 2-pyrrolecarbaldehyde in DMF at room temperature for 7 h to give ethyl 3-phenyl-3*H*-cyclopenta[*a*]-pyrrole-2-dithiocarboxylate (**36**) albeit in low yield (25%) as an unstable dark red liquid together with an unidentified mixture of several products (eq 4).

Conclusion. We note the following results from this investigation: (i) phosphonoketene dithioacetals unsub-

(18) For a review of dithiocarboxylic acid esters (dithioesters), see: (a) Kato, S.; Ishida, M. *Sulfur Rep.* **1988**, *8(4)*, 155. For the synthesis of dithioester (non α, *β*-olefinic) *via* ketene dithioacetal, see for example: (b) Beslin, P.; Perrio, S. *Phosphorus Sulfur Silicon Relat. Elem.* **1994**, *95 and 96*, 383. (c) Saquet, M.; Thuillier, A. *Tetrahedron Lett.* **1980**, *21*, 2165. (d) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Montanucci, M. *J. Org. Chem.* **1983**, *48*, 4795. (e) Ogura, K.; Itoh, Y.; Tsuchihashi, G. *Synthesis* **1980**, 736. For the synthesis of α,*β*-unsaturated dithioesters, see for example: (f) Gosselin, P.; Masson, S.; Thuillier, A. *Tetrahedron Lett.* **1978**, 2717. (g) Hartke, K.; Kunze, O.; Hoederath, W. *Synthesis* **1985**, 960. (h) Masson, S.; Thuillier, A. *Tetrahedron Lett.* **1982**, *23*, 4087.

(19) For the synthesis of 3*H*-cyclopenta[*a*]pyrrole-2-carboxylate *via* similar reaction of α-phosphonoacrylates with pyrrole-2-carbaldehyde, see: (a) Minami, T.; Suganuma, H.; Agawa, T. *Chem. Lett.* **1978**, 285. (b) Flitsch, W.; Lubisch, W. *Chem. Ber.* **1984**, *117*, 1424.

(20) (a) Kametani, T.; Takahashi, K. *Heterocycles* **1978**, *9*, 293. (b) Franck, R. W. *Fortschr. Chem. Org. Naturst.* **1979**, *38*, 1.



stituted at the α-position to phosphorus have been prepared in high yields using organoaluminum chlorides; (ii) 2,2-dithio-1-phosphonovinyl anions were reacted with aldehydes to provide allylic alcohols, and this is the first example of the reaction of 1-phosphonovinyl anion; (iii) dithioallenes have been synthesized from the corresponding allylic alcohols *via* the intramolecular Horner−Emmons−Wittig reaction, and the reactivities of the allene have been discussed; (iv) an effective method for the synthesis of α-phosphonodithioacrylic acid esters has been provided.

Experimental Section

Materials. Dichloromethane was distilled from P_2O_5. THF was distilled from sodium benzophenone ketyl in a recycling still. Dimethylformamide (DMF), diisopropylamine (DIA), and 2,2,6,6-tetramethylpiperidine (TMP) were refluxed with CaH_2 and then distilled. Commercial solution of Me_2AlCl (1.00 M), Et_3Al (0.98 M), Me_3Al (1.00 M), $EtAlCl_2$ (0.96 M), and Et_2AlCl (0.95 M) in hexane were used.

General. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a JEOL JNM-FX-60 or JEOL JNM-FX-α500, operating ^1H NMR at 59.8 or 500.00, and ^{13}C NMR at 15.0 or 125.65 MHz, with Me_4Si as an internal standard. IR spectra were recorded with a Shimadzu IR-408 or a JASCO IR Report-100 instrument. Mass spectra were obtained on a JEOL DX-300 spectrometer. Melting points were measured in open capillary tubes and are not corrected.

General Procedure for the Preparation of Phosphonoketene Dithioacetals 3a−e. Dithiol **2a**,**b** (2.00 mmol), or ethanethiol **2c** (4.00 mmol) was added dropwise to a solution of aluminum reagent (4.00 mmol) in CH_2Cl_2 (10 mL) under a nitrogen atmosphere. After the solution was stirred for 30 min, a solution of phosphonoacetate **1a** or **1b** (1.00 mmol) in CH_2Cl_2 (10 mL) was added, and the mixture was stirred for 4−12 h. The reaction was quenched by a slow addition of water, followed by 4% aqueous HCl. The organic layer was extracted with Et_2O, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel (eluent: AcOEt), giving **3a**, **3b**, **3c**, **3d**, or **3e**. The reaction conditions and yields of **3a−e** were summarized in Table 1. The compounds **3a−e** had the following properties.

Diethyl (1,3-dithian-2-ylidenemethyl)phosphonate (3a): colorless oil; IR (neat) 1515, 1225 cm^{-1}; ^1H NMR (59.8 MHz) δ 1.33 (6 H, t, J = 7.2 Hz), 1.88−2.40 (2 H, m), 2.99 (4 H, t, J = 6.2 Hz), 4.09 (4 H, dq, $^3J_{P-H}$ = 7.0 Hz, J = 7.2 Hz) 5.77 (1 H, d, $^2J_{P-H}$ = 12.3 Hz); ^{13}C NMR (15.0 MHz) δ 16.2 (d, $^3J_{P-C}$ = 6.8 Hz), 22.6, 28.4, 28.6, 61.6 (d, $^2J_{P-C}$ = 5.1 Hz), 108.7 (d, $^1J_{P-C}$ = 199.5 Hz), 159.5 (d, $^2J_{P-C}$ = 6.9 Hz); MS m/z 268 (M^+). Anal. Calcd for $C_9H_{17}O_3PS_2$: C, 40.29; H, 6.39%. Found: C, 39.99; H, 6.40%.

Diethyl (1,3-dithiolan-2-ylidenemethyl)phosphonate (3b): colorless oil; IR (neat) 1395, 1160 cm^{-1}; ^1H NMR (59.8 MHz) δ 1.33 (6 H, t, J = 7.2 Hz), 3.47 (4 H, brs), 4.08 (4 H, dq, $^3J_{P-H}$ = 7.0 Hz, J = 7.2 Hz), 5.63 (1 H, d, $^2J_{P-H}$ = 10.7 Hz); ^{13}C NMR (15.0 MHz) δ 16.0 (d, $^3J_{P-C}$ = 6.0 Hz), 36.9, 39.3, 61.0 (d, $^2J_{P-C}$ = 5.2 Hz), 97.4 (d, $^1J_{P-C}$ = 198.6 Hz), 164.2 (d, $^2J_{P-C}$ = 7.8 Hz); MS m/z 254 (M^+). Anal. Calcd for $C_8H_{15}O_3PS_2$: C, 37.79; H, 5.95%. Found: C, 37.54; H, 5.76%.

Diethyl [2,2-Bis(ethylthio)vinyl]phosphonate (3c): colorless oil; IR (neat) 1525, 1445 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.33 (3 H, t, J = 7.3 Hz), 1.34 (3 H, t, J = 7.3 Hz), 1.35 (6 H, t, J = 7.0 Hz), 2.85 (2 H, q, J = 7.3 Hz), 3.02 (2 H, q, J = 7.3 Hz), 4.09−4.15 (4 H, m), 5.53 (1 H, d, $^2J_{P-H}$ = 11.3 Hz); ^{13}C NMR (125.65 MHz) δ 12.6, 14.6, 16.2 (d, $^3J_{P-C}$ = 7.2 Hz), 27.6, 27.7, 61.6 (d, $^2J_{P-C}$ = 5.2 Hz), 108.3 (d, $^1J_{P-C}$ = 197.6 Hz), 157.5 (d, $^2J_{P-C}$ = 6.2 Hz); MS m/z 284 (M^+). Anal. Calcd for $C_{10}H_{21}O_3PS_2$: C, 42.24; H, 7.44%. Found: C, 41.99; H, 7.47%.

(1,3-Dithian-2-ylidenemethyl)diphenylphosphine oxide (3d): colorless crystal; mp 141−143 °C; IR (KBr) 1250, 1190 cm^{-1}; ^1H NMR (59.8 MHz) δ 1.97−2.32 (2 H, m), 2.87 (2 H, dd, J = 8.8, 6.5 Hz), 2.98 (2 H, dd, J = 8.8, 6.5 Hz), 6.26 (1 H, d, $^2J_{P-H}$ = 18.5 Hz), 7.27−7.94 (5 H, m); ^{13}C NMR (15.0 MHz) δ 22.5, 28.4, 28.7, 113.6 (d, $^1J_{P-C}$ = 106.6 Hz), 128.2 (d, $^3J_{P-C}$ = 12.9 Hz), 130.8 (d, $^2J_{P-C}$ = 10.3 Hz), 131.2, 134.2 (d, $^1J_{P-C}$ = 107.4 Hz), 160.5 (d, $^2J_{P-C}$ = 2.6 Hz); MS m/z 332 (M^+). Anal. Calcd for $C_{17}H_{17}OPS_2$: C, 61.44; H, 5.16%. Found: C, 61.50; H, 5.31%.

(1,3-Ditholan-2-ylidenemethyl)diphenylphosphine oxide (3e): colorless crystal; mp 184.5−185.5 °C; IR (KBr) 1525, 1445, 1180 cm^{-1}; ^1H NMR (59.8 MHz) δ 3.35 (4 H, brs), 6.13 (1 H, d, $^2J_{P-H}$ = 18.0 Hz), 7.33−7.92 (10 H, m); ^{13}C NMR (15.0 MHz) δ 36.6, 39.8, 101.7 (d, $^1J_{P-C}$ = 109.2 Hz), 128.1, 130.6 (d, $^2J_{P-C}$ = 10.3 Hz), 131.2, 133.6 (d, $^1J_{P-C}$ = 106.6 Hz), 163.4 (d, $^2J_{P-C}$ = 2.6 Hz); MS m/z 318 (M^+). Anal. Calcd for $C_{15}H_{16}OPS_2$: C, 60.36 ; H, 4.74%. Found: C, 60.40 ; H, 4.68%.

General Procedure for the Preparation of Diethyl [1-(1,3-Dithiolan-2-ylidene)-2-hydroxyethyl]phosphonates 4−7. To a solution of lithium tetramethylpiperidide (LTMP)(1.76 mmol), generated *in situ* from TMP (0.249 g, 1.76 mmol) and *n*-BuLi (1.64 M in hexane, 1.20 mL, 1.97 mmol) in THF (3 mL) at −78 °C for 30 min, was added a solution of **3c** (0.361 g, 1.42 mmol) at −78 °C. After being stirred for 30 min at this temperature, a solution of aldehyde (1.80 mmol) in THF (4 mL) was added. After the mixture was stirred for 0.8−2 h, the reaction was quenched by the addition of saturated aqueous NH_4Cl, extracted with AcOEt, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel (AcOEt) to give **4**, **5**, **6**, or **7**. The reaction conditions and yields of **4−7** were summarized in Table 2. The compounds **4−7** had the following properties.

Diethyl [1-(1,3-dithiolan-2-ylidene)-2-hydroxy-3,3-dimethylbutyl]phosphonate (4): viscous oil; IR (KBr) 3350, 1510, 1265 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.02 (9 H, s), 1.35 (3 H, t, J = 7.0 Hz), 1.38 (3 H, t, J = 7.0 Hz), 3.26−3.46 (4 H, m), 3.94−4.23 (4 H, m), 4.31 (1 H, dd, $^3J_{P-H}$ = 29.5 Hz, J = 11.1 Hz), 5.11 (1 H, d, J = 11.1 Hz); ^{13}C NMR (125.65 MHz) δ 16.1 (d, $^3J_{P-C}$ = 7.2 Hz), 16.3 (d, $^3J_{P-C}$ = 6.2 Hz), 27.0, 36.9, 38.6, 39.0, 62.2 (d, $^2J_{P-C}$ = 6.2 Hz), 85.8 (d, $^2J_{P-C}$ = 7.2 Hz), 114.2 (d, $^1J_{P-C}$ = 179.0 Hz), 160.3 (d, $^2J_{P-C}$ = 10.3 Hz) ; MS m/z 322 ($M^+ - H_2O$). Anal. Calcd for $C_{13}H_{25}O_4PS_2$: C, 45.86; H, 7.40%. Found: C, 45.94; H, 7.31%.

Diethyl [1-(1,3-dithiolan-2-ylidene)-2-hydroxy-3-methylbutyl]phosphonate (5): colorless crystal; mp 96.5−98.0 °C; IR (KBr) 3325, 1515, 1280 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.90 (3 H, d, J = 6.5 Hz), 1.08 (3 H, d, J = 6.5 Hz), 1.36 (6 H, t, J = 7.0 Hz), 1.68−2.46 (1 H, m), 3.40 (4 H, brs), 3.64−4.46 (6 H, m); ^{13}C NMR (15.0 MHz) δ 16.1 (d, $^3J_{P-C}$ = 6.8 Hz), 16.2 (d, $^3J_{P-C}$ = 6.1 Hz), 16.1, 19.5, 35.2, 36.8, 38.4, 61.9 (d, $^2J_{P-C}$ = 4.7 Hz), 83.2 (d, $^2J_{P-C}$ = 7.7 Hz), 115.6 (d, $^1J_{P-C}$ = 178.8 Hz), 158.3 (d, $^2J_{P-C}$ = 10.4 Hz); MS m/z 308 ($M^+ - H_2O$). Anal. Calcd for $C_{12}H_{23}O_4PS_2$: C, 44.16; H, 7.10%. Found : C, 44.06; H, 6.97%.

Diethyl [2-cyclohexyl-1-(1,3-dithiolan-2-ylidene)-2-hydroxyethyl]phosphonate (6): colorless crystal; mp 83.0−84.5 °C; IR (KBr) 3320, 1515, 1225 cm^{-1}; ^1H NMR (500.00 MHz) δ 0.95−1.04 (2 H, m), 1.09−1.28 (3 H, m), 1.36 (3 H, t, J = 7.2 Hz), 1.37 (3 H, t, J = 7.2 Hz), 1.62−1.65 (2 H, m), 1.71−1.77 (3 H, m), 2.21 (1 H, d, J = 12.8 Hz), 3.30−3.35 (1 H, m), 3.39−3.47 (3 H, m), 4.01−4.18 (6 H, m); ^{13}C NMR (125.65 MHz) δ 16.0 (d, $^3J_{P-C}$ = 7.2 Hz), 16.2 (d, $^3J_{P-C}$ = 6.2 Hz), 25.7, 26.0, 26.3, 29.3, 29.8, 36.7, 38.3, 44.5, 61.8 (d, $^2J_{P-C}$ = 6.2 Hz), 61.9 (d, $^2J_{P-C}$ = 4.1 Hz), 82.1 (d, $^2J_{P-C}$ = 8.3 Hz), 115.3 (d, $^1J_{P-C}$ = 179.0 Hz) 158.2 (d, $^2J_{P-C}$ = 10.4 Hz) ; MS m/z 348 ($M^+ - H_2O$). Anal. Calcd for $C_{15}H_{27}O_4PS_2$: C, 49.17; H, 7.44%. Found: C, 49.04; H, 7.26%.

Diethyl [1-(1,3-dithiolan-2-ylidene)-2-hydroxy-2-phenylethyl]phosphonate (7): colorless crystal; mp 101−102 °C; IR (KBr) 3275, 1520, 1230 cm^{-1}; ^1H NMR (59.8 MHz) δ 1.09 (3 H, t, J = 7.0 Hz), 1.32 (3 H, t, J = 7.0 Hz), 3.41 (4 H, brs), 3.10−4.41 (4 H, m), 4.96−6.16 (2 H, m), 7.01−7.76 (5 H, m); ^{13}C NMR (15.0 MHz) δ 16.0 (d, $^3J_{P-C}$ = 6.9 Hz), 37.0, 38.6,

61.8 (d, $^2J_{P-C}$ = 4.3 Hz), 62.0 (d, $^2J_{P-C}$ = 4.3 Hz), 77.4 (d, $^2J_{P-C}$ = 7.7 Hz), 115.9 (d, $^1J_{P-C}$ = 179.6 Hz), 125.6, 126.9, 127.9, 142.8, 159.1 (d, $^2J_{P-C}$ = 11.2 Hz); MS *m/z* 360 (M^+). Anal. Calcd for $C_{15}H_{21}O_4PS_2$: C, 49.99; H, 5.87%. Found: C, 50.04; H, 5.75%.

Rearrangement of 3a,c,d to 10a,c,d. General Procedure. To a solution of LTMP (0.36 mmol), generated *in situ* from TMP (55 mg, 0.39 mmol) and *n*-BuLi (1.64 M in hexane, 0.22 mL, 0.36 mmol) in THF (3 mL) at −78 °C for 40 min, was added a solution of **3a**, **3c**, or **3d** (0.30 mmol) in THF (2.0 mL) at −78 °C. After the reaction mixture was stirred for 1 h, the reaction was quenched by the addition of water, extracted with AcOEt, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by preparative TLC (AcOEt:hexane = 4:1) to give **10a**, **10c**, or **10d**. The compounds **10a**,**c**,**d** had the following properties.

Diethyl (6,7-dihydro-5*H*-1,4-dithiepin-2-yl)phosphonate (10a): yield 40 mg (0.15 mmol, 50%); colorless oil; IR (neat) 1240 cm^{-1}; ^{1}H NMR (59.8 MHz) δ 1.35 (6 H, t, J = 7.2 Hz), 1.92−2.44 (2 H, m), 3.32−3.72 (4 H, m), 4.10 (4 H, dq, $^3J_{P-H}$ = 7.0 Hz, J = 7.2 Hz), 7.03 (1 H, d, $^3J_{P-H}$ = 19.7 Hz); ^{13}C NMR (15.0 MHz) δ 16.2 (d, $^3J_{P-C}$ = 6.9 Hz), 30.0, 33.7, 34.1, 62.5 (d, $^2J_{P-C}$ = 5.3 Hz), 121.5 (d, $^1J_{P-C}$ = 186.5 Hz), 137.4 (d, $^2J_{P-C}$ = 17.2 Hz); HRMS calcd for $C_9H_{17}O_3PS_2$, 260.0407. Found 260.0358. Anal. Calcd for $C_9H_{17}O_3PS_2$: C, 40.29; H, 6.32%. Found: C, 40.42; H, 6.42%.

Diethyl [(*Z*)-1,2-bis(ethylthio)vinyl]phosphonate (10c): yield 42 mg (0.15 mmol, 50%); colorless oil; IR (neat) 1250 cm^{-1}; ^{1}H NMR (500.00 MHz) δ 1.27 (3 H, t, J = 7.3 Hz), 1.34 (6 H, t, J = 7.0 Hz), 1.37 (3 H, t, J = 7.3 Hz), 2.80−2.91 (4 H, m), 3.99−4.18 (4 H, m), 7.90 (1 H, d, $^3J_{P-H}$ = 15.6 Hz); ^{13}C NMR (125.65 MHz) δ 14.7, 15.6, 16.3 (d, $^3J_{P-C}$ = 6.2 Hz), 27.9, 28.2, 62.2 (d, $^2J_{P-C}$ = 5.2 Hz), 115.1 (d, $^1J_{P-C}$ = 194.5 Hz), 157.2 (d, $^2J_{P-C}$ = 24.8 Hz); HRMS calcd for $C_{10}H_{21}O_3PS_2$, 284.0669 (M^+), found 284.0651.

6,7-Dihydro-5*H*-1,4-dithiepin-2-yldiphenylphosphine oxide (10d): yield 45 mg (0.14 mmol, 47%); colorless crystal; mp 152−153 °C; IR (KBr) 1520, 1425, 1180 cm^{-1}; ^{1}H NMR (59.8 MHz) δ 1.84−2.44 (2 H, m), 3.24−3.76 (4 H, m), 7.04 (1 H, d, $^3J_{P-H}$ = 16.8 Hz), 7.47−7.97 (10 H, m); ^{13}C NMR (15.0 MHz) δ 29.9, 30.2, 34.6 (d, $^3J_{P-C}$ = 5.2 Hz), 127.1 (d, $^1J_{P-C}$ = 12.0 Hz), 128.3 (d, $^3J_{P-C}$ = 12.0 Hz), 131.1 (d, $^1J_{P-C}$ = 107.5 Hz), 132.0 (d, $^2J_{P-C}$ = 9.5 Hz), 132.0, 137.9 (d, $^2J_{P-C}$ = 14.7 Hz); HRMS calcd for $C_{17}H_{17}OPS_2$, 332.0461, found 332.0460. Anal. Calcd for $C_{17}H_{17}OPS_2$: C, 61.43; H, 5.15%. Found: C, 61.55; H, 5.26%.

General Procedure for the Preparation of Diethyl [1-(1,3-dithian-2-ylidene)-2-hydroxyethyl]phosphonates 11−14. To a solution of LDA (1.64 mmol), generated *in situ* from DIA (0.166 g, 1.64 mmol) and *n*-BuLi (1.64 M in hexane, 1.00 mL, 1.64 mmol) in THF (3 mL) at −78 °C for 30 min, was added a solution of **3a** (0.301 g, 1.12 mmol) and aldehyde (1.50 mmol) in THF (4 mL) at −78 °C. After the mixture was stirred for 1.5 h, the reaction was quenched by the addition of saturated aqueous NH_4Cl, extracted with AcOEt or CH_2Cl_2, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel (AcOEt) to afford **11**, **12**, **13**, or **14**. The reaction conditions and yields of **11**−**14** were summarized in Table 3. The compounds **11**−**14** had the following properties.

Diethyl [1-(1,3-dithian-2-ylidene)-2-hydroxy-3,3-dimethylbutyl]phosphonate (11): colorless crystal; mp 95.5−96.5 °C; IR (KBr) 3300, 1490, 1305 cm^{-1}; ^{1}H NMR (59.8 MHz) δ 1.01 (9 H, s), 1.36 (6 H, t, J = 7.0 Hz), 1.80−2.40 (2 H, m), 2.56−3.40 (4 H, m), 3.80−5.48 (6 H, m); ^{13}C NMR (15.0 MHz) δ 16.2 (d, $^3J_{P-C}$ = 6.0 Hz), 23.5, 27.2, 29.3, 29.3, 38.5, 62.1 (d, $^2J_{P-C}$ = 6.9 Hz), 80.7 (d, $^2J_{P-C}$ = 7.7 Hz), 124.8 (d, $^1J_{P-C}$ = 175.4 Hz), 156.4 (d, $^2J_{P-C}$ = 9.5 Hz); MS *m/z* 336 (M^+). Anal. Calcd for $C_{14}H_{27}O_4PS_2$: C, 47.44; H, 7.68%. Found: C, 47.54; H, 7.56%.

Diethyl [1-(1,3-dithian-2-ylidene)-2-hydroxy-3-methylbutyl]phosphonate (12): colorless crystal; mp 115−116 °C; IR (KBr) 3300, 1505, 1215 cm^{-1}; ^{1}H NMR (59.8 MHz) δ 0.87 (3 H, d, J = 6.5 Hz), 1.09 (3 H, d, J = 6.5 Hz), 1.36 (6 H, t, J = 7.1 Hz), 1.72−2.44 (3 H, m), 2.56−3.32 (4 H, m), 3.76−4.92 (6 H, m); ^{13}C NMR (15.0 MHz) δ 16.1 (d, $^3J_{P-C}$ = 6.9 Hz), 16.2 (d, $^3J_{P-C}$ = 6.9 Hz), 19.1, 19.5, 23.3, 28.9, 28.9, 34.9, 78.4 (d, $^2J_{P-C}$ = 7.7 Hz), 125.5 (d, $^1J_{P-C}$ = 174.5 Hz), 154.8 (d, $^2J_{P-C}$ = 9.5 Hz); MS *m/z* 332 (M^+). Anal. Calcd for $C_{13}H_{25}O_4PS_2$: C, 45.87; H, 7.40%. Found: C, 45.77; H, 7.16%.

Diethyl [2-cyclohexyl-1-(1,3-dithian-2-ylidene)-2-hydroxyethyl]phosphonate (13): colorless crystal; mp 111−112 °C; IR (KBr) 3275, 1500, 1220 cm^{-1}; ^{1}H NMR (59.8 MHz) δ 0.52−1.92 (10 H, m), 1.36 (6 H, t, J = 7.1 Hz), 1.92−2.44 (3 H, m), 2.56−3.48 (4 H, m), 3.76−4.94 (6 H, m); ^{13}C NMR (15.0 MHz) δ 15.8 (d, $^3J_{P-C}$ = 6.0 Hz), 16.0 (d, $^3J_{P-C}$ = 6.0 Hz), 23.1, 25.7, 25.9, 26.2, 28.7, 28.7, 29.3, 29.7, 44.2, 61.5 (d, $^2J_{P-C}$ = 5.2 Hz), 77.1 (d, $^2J_{P-C}$ = 7.7 Hz), 125.5 (d, $^1J_{P-C}$ = 174.5 Hz), 154.0 (d, $^2J_{P-C}$ = 9.5 Hz); MS *m/z* 362 ($M^+ - H_2O$). Anal. Calcd for $C_{16}H_{22}O_4PS_2$: C, 50.50; H, 7.68%. Found: C, 50.60; H, 7.49%.

Diethyl [1-(1,3-dithian-2-ylidene)-2-hydroxy-2-phenylethyl]phosphonate (14): colorless crystal; mp 118−119 °C; IR (KBr) 3225, 1500, 1200 cm^{-1}; ^{1}H NMR (59.8 MHz) δ 1.07 (3 H, t, J = 6.9 Hz), 1.35 (3 H, t, J = 6.9 Hz), 1.72−2.44 (2 H, m), 2.72−3.28 (4 H, m), 3.30−4.36 (4 H, m), 5.36−6.44 (2 H, m), 7.08−7.60 (5 H, m); ^{13}C NMR (15.0 MHz) δ 16.0 (d, $^3J_{P-C}$ = 6.0 Hz), 23.2, 28.9, 28.9, 61.7 (d, $^2J_{P-C}$ = 5.1 Hz), 73.0 (d, $^2J_{P-C}$ = 7.7 Hz), 125.4, 125.5 (d, $^1J_{P-C}$ = 174.5 Hz), 126.7, 127.8, 143.0, 155.3 (d, $^2J_{P-C}$ = 9.4 Hz); HRMS calcd for $C_{16}H_{23}O_4PS_2$, 374.0793 (M^+), found 374.0821. Anal. Calcd for $C_{16}H_{23}O_4PS_2$: C, 51.32; H, 6.06%. Found: C, 51.35; H, 6.19%.

General Procedure for the Preparation of Diethyl [1-[bis(ethylthio)methylene]-2-hydroxyethyl]phosphonates 15−18. To a solution of LTMP (1.10 mmol), generated *in situ* from TMP (0.170 g, 1.20 mmol) and *n*-BuLi (1.64 M in hexane, 0.671 mL, 1.10 mmol) in THF (6 mL) at −78 °C for 40 min, was added a solution of **3c** (0.284 g, 1.00 mmol) and aldehyde (1.50 mmol) in THF (3 mL) at this temperature. After the mixture was stirred for 1.5−2 h, the reaction was quenched by the addition of saturated aqueous NH_4Cl, extracted with AcOEt, washed with brine, dried over Na_2SO_4, and then concentrated *in vacuo*. The residue was chromatographed on silica gel (AcOEt:hexane = 2:1) to afford **15**, **16**, **17**, or **18**. The reaction conditions and yields of **15**−**18** were summarized in Table 3. The compounds **15**−**18** had the following properties.

Diethyl [1-[bis(ethylthio)methylene]-2-hydroxy-3,3-dimethylbutyl]phosphonate (15): colorless oil; IR (neat) 3350, 1495, 1205 cm^{-1}; ^{1}H NMR (500.00 MHz) δ 1.01 (9 H, s), 1.257 (3 H, t, J = 7.3 Hz), 1.259 (3 H, t, J = 7.3 Hz), 1.34 (3 H, t, J = 7.1 Hz), 1.37 (3 H, t, J = 7.1 Hz), 2.66−2.76 (2 H, m), 2.96−3.09 (2 H, m), 4.01−4.16 (2 H, m), 4.16−4.28 (2 H, m), 5.03 (1 H, dd, $^3J_{P-H}$ = 29.9 Hz, J = 7.6 Hz), 5.32 (1 H, d, J = 10.4 Hz); ^{13}C NMR (125.65 MHz) δ 15.0, 15.1, 16.2 (d, $^3J_{P-C}$ = 6.2 Hz), 16.3 (d, $^3J_{P-C}$ = 7.2 Hz), 27.4, 29.2, 30.1, 38.3, 62.7 (d, $^2J_{P-C}$ = 5.2 Hz), 81.6 (d, $^2J_{P-C}$ = 8.3 Hz), 138.9 (d, $^1J_{P-C}$ = 168.63 Hz), 152.3 (d, $^2J_{P-C}$ = 8.3 Hz); MS *m/z* 371 (M^+). Anal. Calcd for $C_{15}H_{31}O_4PS_2$: C, 48.63; H, 8.43%. Found: C, 48.54; H, 8.06%.

Diethyl [1-[bis(ethylthio)methylene]-2-hydroxy-3-methylbutyl]phosphonate (16): colorless oil; IR (neat) 3400, 1510, 1210 cm^{-1}; ^{1}H NMR (500.00 MHz) δ 0.84 (3 H, d, J = 6.7 Hz), 1.11 (3 H, d, J = 6.7 Hz), 1.27 (6 H, t, J = 7.3 Hz), 1.34−1.38 (6 H, m), 2.11 (1 H, dq, J = 16.5, 6.7 Hz), 2.69−2.78 (2 H, m), 2.95−3.05 (2 H, m), 4.05−4.23 (4 H, m), 4.80 (1 H, dd, $^3J_{P-H}$ = 29.6 Hz, J = 9.7 Hz); ^{13}C NMR (125.65 MHz) δ 14.9, 14.9, 16.1 (d, $^3J_{P-C}$ = 7.2 Hz), 16.4 (d, $^3J_{P-C}$ = 7.2 Hz), 19.4, 19.5, 28.7, 29.3, 34.6, 62.1 (d, $^2J_{P-C}$ = 7.2 Hz), 62.2, 79.8 (d, $^2J_{P-C}$ = 9.3 Hz), 139.6 (d, $^1J_{P-C}$ = 168.6 Hz), 150.5 (d, $^2J_{P-C}$ = 8.3 Hz); MS *m/z* 313 ($M^+ - CH(CH_3)_2$). Anal. Calcd for $C_{14}H_{29}O_4PS_2$: C, 47.17; H, 8.20%. Found: C, 47.02; H, 8.06%.

Diethyl [1-[bis(ethylthio)methylene]-2-cyclohexyl-2-hydroxyethyl]phosphonate (17): colorless oil; IR (neat) 3400, 1510, 1210 cm^{-1}; ^{1}H NMR (500.00 MHz) δ 0.93−1.06 (2 H, m), 1.13−1.19 (2 H, m), 1.26 (3 H, t, J = 7.3 Hz), 1.27 (3 H, t, J = 7.3 Hz), 1.35 (3 H, t, J = 7.1 Hz), 1.36 (3 H, t, J = 7.1 Hz), 1.43−1.46 (3 H, m), 1.65−1.84 (4 H, m), 2.24 (1 H, d, J = 12.2 Hz), 2.69−2.77 (2 H, m), 2.99 (2 H, dq, J = 13.7, 7.3 Hz), 4.05−4.22 (4 H, m), 4.85 (1 H, dd, $^3J_{P-H}$ = 29.6 Hz, J = 9.6 Hz); ^{13}C NMR (125.65 MHz); δ 15.0, 15.1, 16.2 (d, $^3J_{P-C}$ = 6.2 Hz), 16.5 (d, $^3J_{P-C}$ = 6.2 Hz), 26.0, 26.3, 26.5, 28.8, 29.4, 29.8, 30.1, 44.0, 62.1 (d, $^2J_{P-C}$ = 6.2 Hz), 62.2 (d, $^2J_{P-C}$ = 5.2 Hz),

78.9 (d, $^2J_{P-C}$ = 8.3 Hz), 139.4 (d, $^1J_{P-C}$ = 167.6 Hz), 150.5 (d, $^2J_{P-C}$ = 9.3 Hz); MS *m*/*z* 379 ($M^+ - H_2O$). Anal. Calcd for $C_{17}H_{33}O_4PS_2$: C, 51.49; H, 8.38%. Found: C, 51.31; H, 8.26%.

Diethyl [1-[bis(ethylthio)methylene]-2-hydroxy-2-phenylethyl]phosphonate (18): colorless oil; IR (neat) 3350, 1510, 1200 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.10 (3 H, t, *J* = 7.2 Hz), 1.32 (6 H, t, *J* = 7.1 Hz), 1.34 (3 H, t, *J* = 7.2 Hz), 2.78−2.88 (2 H, m), 3.04 (1 H, dq, *J* = 13.1, 7.2 Hz), 3.08 (1 H, dq, *J* = 13.1, 7.2 Hz), 3.60 (1 H, dq, $^3J_{P-H}$ = 10.2 Hz, *J* = 7.1 Hz), 3.61 (1 H, dq, $^3J_{P-H}$ = 10.1 Hz, *J* = 7.1 Hz), 3.71 (2 H, dq, $^3J_{P-H}$ = 10.2 Hz, *J* = 7.1 Hz), 4.05 (1 H, dq, $^3J_{P-H}$ = 10.2 Hz, *J* = 7.1 Hz), 4.07 (1 H, dq, $^3J_{P-H}$ = 10.2 Hz, *J* = 7.1 Hz), 4.10−4.18 (2 H, m), 5.45 (1 H, d, *J* = 11.7 Hz), 6.43 (1 H, dd, $^3J_{P-H}$ = 27.8 Hz, *J* = 11.7 Hz), 7.20−7.42 (5 H, m); ^{13}C NMR (125.65 MHz) δ 15.0, 15.0, 16.1, 16.2 (d, $^3J_{P-C}$ = 6.2 Hz), 28.9, 29.4, 62.1 (d, $^2J_{P-C}$ = 5.2 Hz), 62.1 (d, $^2J_{P-C}$ = 5.2 Hz), 74.7 (d, $^2J_{P-C}$ = 8.3 Hz), 125.5, 126.9, 128.1, 139.0 (d, $^1J_{P-C}$ = 168.6 Hz), 142.8, 151.2 (d, $^2J_{P-C}$ = 8.3 Hz); MS *m*/*z* 390 (M^+). Anal. Calcd for $C_{17}H_{27}O_4PS_2$: C, 52.02; H, 7.45%. Found: C, 52.26; H, 7.08%.

The Horner−Emmons−Wittig Reaction of Allylic Alcohols 4−6, and 11−13. General Procedure. To a suspension of *t*-BuOK (0.123 g, 1.10 mmol) in THF (8 mL) was added a solution of **4**, **5**, **6**, **11**, **12**, or **13** (1.00 mmol) in THF (6 mL) at room temperature. After the solution was stirred for 4−12 h, the reaction was quenched by the addition of saturated aqueous NH_4Cl, extracted with AcOEt, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel (Et_2O:hexane = 1:20) to give corresponding symmetrical dimers **20**−**22** or mixtures of symmetrical and unsymmetrical dimers **23a**,**b**, **24a**,**b**, or **25a**,**b**. Each of pure compounds **23a**,**b** and **25a**,**b** was separated by fractional recrystallization of the mixtures from heptane. Attempts to obtain pure **24a** and **24b** from the mixture were unsuccessful. The reaction conditions, yields, and ratios of symmetrical dimers to unsymmetrical dimers were summarized in Table 4. The compounds **20**−**22**, **23a**,**b**, **24a**,**b**, and **25a**,**b** had the following properties.

(11*Z*,12*Z*)-11,12-Dineopentylidene-1,4,7,10-tetrathiodispiro[4.0.4.2]dodecane (20): colorless crystal; mp 155−156 °C; IR (KBr) 1480, 1280 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.24 (18 H, s), 3.14−3.26 (8 H, m), 5.63 (2 H, s); ^{13}C NMR (125.65 MHz) δ 30.9, 33.6, 40.1, 82.5, 131.8, 138.6; MS *m*/*z* 372 (M^+). Anal. Calcd for $C_{18}H_{28}S_4$: C, 58.01; H, 7.57%. Found: C, 57.88; H, 7.67%.

(11*Z*,12*Z*)-11,12-Diisobutylidene-1,4,7,10-tetrathiodispiro[4.0.4.2]dodecane (21): colorless crystal; mp 128−129 °C; IR (KBr) 1470, 1275 cm^{-1}; ^1H NMR (59.8 MHz) δ 1.02 (12 H, d, *J* = 6.7 Hz), 2.68−3.52 (10 H, m), 5.46 (2 H, d, *J* = 10.4 Hz); ^{13}C NMR (15.0 MHz) δ 22.8, 27.0, 40.4, 81.2, 131.1, 137.3; MS *m*/*z* 344 (M^+). Anal. Calcd for $C_{16}H_{24}S_4$: C, 55.77; H, 7.02%. Found: C, 56.03; H, 7.11%.

(11*Z*,12*Z*)-11,12-Bis(cyclohexylmethylene)-1,4,7,10-tetrathiodispiro[4.0.4.2]dodecane (22): colorless crystal; mp 130−131 °C; IR (KBr) 1450, 1270 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.00−1.08 (4 H, m), 1.16 (2 H, m), 1.28 (4 H, m), 1.63−1.66 (2 H, m), 1.70−1.74 (4 H, m), 1.76−1.79 (4 H, m), 2.69−2.77 (2 H, m), 3.07−3.13 (4 H, m), 3.25−3.31 (4 H, m), 5.51 (2 H, d, *J* = 10.4 Hz); ^{13}C NMR (125.65 MHz) δ 25.9, 26.0, 32.6, 36.6, 40.5, 81.0, 129.6, 138.1; HRMS calcd for $C_{22}H_{32}S_4$, 424.1386 (M^+), found 424.1355. Anal. Calcd for $C_{22}H_{32}S_4$: C, 62.21; H, 7.59%. Found: C, 61.67; H, 7.55%.

(13*Z*,14*Z*)-13,14-Dineopentylidene-1,5,8,12-tetrathiodispiro[5.0.5.2]tetradecane (23a): colorless crystal; mp 180.5−181.5 °C; IR (KBr) 1435, 1410, 1275 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.31 (18 H, s), 2.01−2.10 (2 H, m), 2.16−2.22 (2 H, m), 2.77−2.81 (4 H, m), 3.10 (4 H, ddd, *J* = 14.3, 11.6, 3.4 Hz), 5.73 (2 H, s); ^{13}C NMR (125.65 MHz) δ 23.7, 29.7, 31.7, 33.1, 69.7, 133.4, 138.3; MS *m*/*z* 400 (M^+). Anal. Calcd for $C_{20}H_{32}S_4$: C, 59.94; H, 8.05%. Found: C, 59.86; H, 8.17%.

(*Z*)-3-*tert*-Butyl-2-(1,3-dithian-2-ylidene)-1-neopentylidene-5,9-dithiospiro[3.5]nonane (23b): colorless crystal; mp 130.5−131.0 °C; IR (KBr) 1415, 1280 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.12 (9 H, s), 1.32 (9 H, s), 1.92−2.01 (1 H, m), 2.06−2.18 (3 H, m), 2.71−2.98 (7 H, m), 3.04 (1 H, ddd, *J* = 13.5, 8.5, 5.2 Hz), 3.05 (1 H, s), 5.91 (1 H, s); ^{13}C NMR (125.65 MHz) δ 24.4, 24.7, 29.1 29.3, 29.9, 30.3, 30.4, 31.8, 32.9, 37.8, 56.4, 69.0, 122.4, 138.6 140.6, 142.1; HRMS calcd for $C_{20}H_{32}S_4$, 400.1390 (M^+), found 400.1376. Anal. Calcd for $C_{20}H_{32}S_4$: C, 59.95; H, 8.05%. Found: C, 60.14; H, 7.89%.

(13*Z*,14*Z*)-13,14-Diisobutylidene-1,5,8,12-tetrathiodispiro[5.0.5.2]tetradecane (24a) and (*Z*)-2-(1,3-Dithian-2-ylidene)-1-isobutylidene-3-isopropyl-5,9-dithiospiro[3.5]nonane (24b): colorless crystal; ^1H NMR [for a mixture of **24a** and **24b**](500.00 MHz) δ 0.93 (3 H × 0.23, d, *J* = 6.7 Hz), 1.03 (12 H × 0.77, d, *J* = 6.7 Hz), 1.04 (3 H × 0.23, d, *J* = 6.7 Hz), 1.07 (3 H × 0.23, d, *J* = 6.7 Hz,), 1.28 (3 H × 0.23, d, *J* = 6.7 Hz), 1.90−2.30 (4 H × 0.77, m, and 5 H × 0.23, m), 2.65−3.16 (10 H × 0.77, m, and 10 H × 0.23, m), 5.48 (2 H × 0.77, d, *J* = 10.7 Hz), 5.81 (1 H × 0.23, d, *J* = 10.7 Hz); ^{13}C NMR [for a mixture of **24a** and **24b**](125.65 MHz) δ 19.5, 23.1, 23.5, 23.6, 23.7, 24.2, 24.3, 24.7, 28.0, 28.4, 29.2, 29.2, 29.6, 29.9, 30.4, 56.4, 64.3, 69.4, 122.9, 131.9, 136.3, 137.3, 138.1, 138.7; MS *m*/*z* 372 (M^+). Anal. Calcd for $C_{18}H_{28}S_4$: C, 58.01; H, 7.57%. Found [for a mixture of **24a** and **24b**]: C, 57.93; H, 7.44%.

(13*Z*,14*Z*)-13,14-Bis(cyclohexylmethylene)-1,5,8,12-tetrathiodispiro[5.0.5.2]tetradecane (25a): colorless crystal; mp 177−178 °C; IR (KBr) 1450, 1275 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.01−1.09 (4 H, m), 1.13−1.21 (2 H, m), 1.27−1.37 (4 H, m), 1.64−1.77 (10 H, m), 1.99−2.13 (4 H, m), 2.81 (4 H, dt, *J* = 14.3, 4.9 Hz), 2.85−2.93 (2 H, m), 2.99 (4 H, ddd, *J* = 14.3, 9.8, 4.6 Hz), 5.51 (2 H, d, *J* = 10.7 Hz); ^{13}C NMR (125.65 MHz) δ 23.5, 25.8, 26.0, 29.1, 33.1, 37.4, 69.3, 130.3, 138.9; MS *m*/*z* 452 (M^+). Anal. Calcd for $C_{24}H_{36}S_4$: C, 63.66; H, 8.01%. Found [for a mixture of **25a** and **25b**]: C, 63.50; H, 7.80%.

(*Z*)-3-Cyclohexyl-1-(cyclohexylmethylene)-2-(1,3-dithian-2-ylidene)-5,9-dithiospiro[3.5]nonane (25b): colorless crystal; mp 146−148 °C; IR (KBr) 1450, 1275 cm^{-1}; ^1H NMR (500.00 MHz) δ 0.98−1.42 (10 H, m), 1.64−2.01 (13 H, m), 2.07−2.10 (1 H, m), 2.16 (2 H, dt, *J* = 11.6, 6.7 Hz), 2.69−2.75 (2 H, m), 2.79−2.92 (4 H, m), 2.98 (1 H, dt, *J* = 13.7, 6.7 Hz), 3.01 (1 H, dt, *J* = 13.7, 6.7 Hz), 3.14 (1 H, d, *J* = 1.5 Hz), 5.81 (1 H, d, *J* = 10.7 Hz); ^{13}C NMR (125.65 MHz) δ 24.4, 24.8, 25.6, 25.7, 26.1, 26.4, 26.5, 27.8, 29.2, 29.6, 30.0, 30.3, 37.7, 40.9, 56.6, 64.1, 122.0, 135.8, 137.0, 139.4; MS *m*/*z* 452 (M^+).

Synthesis of 3-*tert*-Butyl-1,1-bis(ethylthio)-1,2-propadiene (26). The reaction was carried out using **15** (0.446 g, 1.20 mmol) and *t*-BuOK (0.149 g, 1.32 mmol) in THF (40 mL) at room temperature for 0.5 h. After similar workup as described above, the product **26** was obtained in a almost pure form in 0.255 g (1.18 mmol, 98%) yield. Further purification of **26** on silica gel or by distillation was unsuccessful due to the ease of decomposition. **26**: colorless oil; IR (neat) 1930 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.08 (9 H, s), 1.29 (6 H, t, *J* = 7.3 Hz), 2.71 (4 H, q, *J* = 7.3 Hz), 5.46 (1 H, s); ^{13}C NMR (125.65 MHz) δ 14.5, 27.9, 29.9, 33.0, 98.8, 108.4, 198.1; MS *m*/*z* 216 (M^+).

Synthesis of 3,3-Bis(ethylthio)-2-neopentylidene-4,4-diphenylcyclobutanone (27). To a solution of the dithioallene **26** (0.273 g, 1.26 mmol) and triethylamine (1.00 mL, 4.91 mmol) in benzene (6 mL) was added dropwise a solution of diphenylacetyl chloride (1.16 g, 5.04 mmol) in benzene (4 mL) at room temperature, and the mixture was stirred for 14 h. After the reaction was quenched by the addition of H_2O and extracted with AcOEt. The extract was washed with brine, dried over Na_2SO_4, and then concentrated *in vacuo*. The residue was chromatographed on silica gel ($CHCl_3$:hexane = 1:1) and then recrystallized from hexane to afford a [2 + 2] cycloadduct **27**: yield 0.339 g (0.826 mmol, 66%); pale yellow crystal; mp 128.5−131 °C; IR (KBr) 1750, 1635, 1500 cm^{-1}; ^1H NMR (500.00 MHz) δ 0.80 (6 H, t, *J* = 7.5 Hz), 1.34 (9 H, s), 2.01 (2 H, dq, *J* = 10.7, 7.5 Hz), 2.14 (2 H, dq, *J* = 10.7, 7.5 Hz), 6.84 (1 H, s), 7.23−7.54 (10 H, m); ^{13}C NMR (125.65 MHz) δ 12.8, 25.9, 29.9, 34.2, 68.6, 84.0, 127.1, 127.4, 129.3, 138.9, 142.7, 148.2, 201.5; MS *m*/*z* 410 (M^+). Anal. Calcd for $C_{25}H_{30}OS_2$: C, 73.12; H, 7.36%. Found: C, 72.99; H, 7.25%.

Acid-Catalyzed Decomposition of a Allylic Alcohol 15. To a solution of **15** (0.100 g, 0.270 mmol) in CH_2Cl_2 (15 mL) was added trifluoromethanesulfonic acid (40.5 mg, 0.270 mmol) at room temperature. After the mixture was stirred at this temperature for 24 h, the reaction was quenched by the

addition of H_2O. The organic layer was extracted with $CHCl_3$, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel (AcOEt:hexane = 1:2) to afford *S*-ethyl (*Z*)-α-(diethylphosphono)-*β*-(*tert*-butyl)thioacrylate (**33**)**:** yield 41 mg (0.144 mmol, 53%); colorless oil; IR (neat) 1675 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.29 (3 H, t, J = 7.4 Hz), 1.31 (9 H, s), 1.33 (6 H, t, J = 7.3 Hz), 2.91 (2 H, q, J = 7.4 Hz), 4.10−4.21 (4 H, m), 6.93 (1 H, d, $^3J_{P-H}$ = 48.2 Hz); ^{13}C NMR (125.65 MHz) δ 14.5, 16.2 (d, $^3J_{P-C}$ = 7.2 Hz), 24.4, 29.9, 35.0 (d, $^3J_{P-C}$ = 5.2 Hz), 62.6 (d, $^2J_{P-C}$ = 6.2 Hz), 132.2 (d, $^1J_{P-C}$ = 180.0 Hz), 165.1 (d, $^2J_{P-C}$ = 7.2 Hz), 193.9 (d, $^2J_{P-C}$ = 13.5 Hz); MS *m*/*z* 309 (M^+). Anal. Calcd for $C_{13}H_{25}O_4PS$: C, 51.07; H, 8.06%. Found: C, 50.63; H, 8.17%.

Synthesis of Ethyl α-(diethylphosphono)dithioacrylates 34 and 35. General Procedure. Method A. To a solution of **15** or **18** (0.270 mmol) and *n*-Bu_4NX (X = Br or I) (2.70 mmol) in CH_2Cl_2 (15 mL) was added trifluoromethanesulfonic acid (40.5 mg, 0.270 mmol) at room temperature. After the mixture was stirred at this temperature for 16−41 h, the reaction was quenched by the addition of H_2O. After similar workup, the residue was chromatographed on silica gel (AcOEt:hexane = 1:2) to afford the dithioacrylate **34** or **35** as orange oil. The reaction conditions and yields were summarized in Table 8.

Method B. To a solution of **15** or **18** (0.270 mmol) in CH_2Cl_2 (5 mL) were added Ph_3P (85.0 mg, 0.324 mmol) and CBr_4 (0.179 g, 0.540 mmol) in turn at room temperature. After the mixture was stirred at this temperature for 61 h, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$. After similar workup, the residue was chromatographed on silica gel to afford the dithioester **34** or **35**. The yields and reaction conditions were summarized in Table 8. The compounds **34** and **35** had the following properties.

Ethyl (*E*)-α-(diethylphosphono)-*β*-*tert*-butyldithioacrylate (34): orange oil; IR (neat) 1250 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.18 (9 H, s), 1.32 (6 H, t, J = 7.2 Hz), 1.35 (3 H, t, J = 7.4 Hz), 3.28 (2 H, q, J = 7.4 Hz), 4.12 (4 H, dq, $^3J_{P-H}$ = 7.2 Hz, J = 7.2 Hz), 6.53 (1 H, d, $^3J_{P-H}$ = 26.6 Hz); ^{13}C NMR (125.65 MHz) δ 11.8, 16.1 (d, $^3J_{P-C}$ = 6.2 Hz), 29.7 (d, $^4J_{P-C}$ = 2.1 Hz), 31.2, 36.8 (d, $^3J_{P-C}$ = 17.6 Hz), 62.6 (d, $^2J_{P-C}$ = 5.2 Hz), 135.7 (d, $^1J_{P-C}$ = 172.8 Hz), 156.0 (d, $^2J_{P-C}$ = 6.2 Hz), 227.5 (d, $^2J_{P-C}$ = 10.3 Hz); MS *m*/*z* 324 (M^+). Anal. Calcd for $C_{13}H_{25}O_3PS_2$: C, 48.13; H, 7.77%. Found: C, 48.41; H, 7.63%.

Ethyl (*E*)-α-(diethylphosphono)-*β*-phenyldithioacrylate (35): orange oil; IR (neat) 1250 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.32 (3 H, t, J = 7.4 Hz), 1.35 (6 H, t, J =7.2 Hz), 3.29 (2 H, q, J = 7.4 Hz), 4.20 (4 H, dq, $^3J_{P-H}$ = 7.0 Hz, J = 7.2 Hz), 7.28−7.40 (3 H, m), 7.47 (1 H, d, $^3J_{P-H}$ = 24.1 Hz), 7.52−7.53 (2 H, m); ^{13}C NMR (125.65 MHz) δ 11.7, 16.1 (d, $^3J_{P-C}$ = 7.2 Hz), 30.8, 62.8, 62.9 (d, $^2J_{P-C}$ = 5.2 Hz), 128.4, 129.9, 130.3, 133.4 (d, $^3J_{P-C}$ = 19.7 Hz), 137.7 (d, $^1J_{P-C}$ = 176.9 Hz), 142.6 (d, $^2J_{P-C}$ = 8.3 Hz), 227.8 (d, $^2J_{P-C}$ = 9.3 Hz); MS *m*/*z* 344 (M^+). Anal. Calcd for $C_{15}H_{21}O_3PS_2$: C, 52.31; H, 6.15%. Found: C, 52.66; H, 6.38%.

Synthesis of Ethyl 3-Phenyl-3*H*-cyclopenta[*a*]pyrrole-2-dithiocarboxylate (36). To a suspension of NaH (60% dispersion in mineral oil, 14.0 mg, 0.351 mmol) in DMF (1.5 mL) was added pyrrole-2-carbaldehyde (33.4 mg, 0.351 mmol) in DMF (1.5 mL) at room temperature. After the solution was stirred at this temperature for 10 min, a solution of **35** (0.100 g, 0.319 mmol) in DMF (3 mL) were added slowly, and the mixture was stirred for 7 h. After similar workup as described above, the mixture was extracted with AcOEt, washed with brine, dried over Na_2SO_4, and then concentrated *in vacuo*. The residue was chromatographed on silica gel (AcOEt:hexane = 1:4) to give **36** (23.0 mg, 0.0810 mmol, 25%) as an unstable dark red viscous oil, of which exposure to air for a short period shows several spots on silica gel. **36**: IR (KBr) 1350, 1250, 1180 cm^{-1}; ^1H NMR (500.00 MHz) δ 1.27 (3 H, t, J = 7.4 Hz), 3.14 (1 H, dq, J = 13.5, 7.4 Hz), 3.24 (1 H, dq, J = 13.5, 7.4 Hz), 6.166−6.168 (1 H, m), 6.33 (1 H, dd, J = 3.7, 2.4 Hz), 6.41 (1 H, ddd, J = 3.7, 0.9, 0.9 Hz), 6.81−6.82 (1 H, m), 7.11−7.13 (2 H, m), 7.24−7.28 (3 H, m), 7.63 (1 H, dd, J = 1.5, 0.6 Hz); ^{13}C NMR (125.65 MHz) δ 12.8, 29.1, 67.9, 106.2, 115.2, 119.7, 124.6, 127.9, 128.2, 128.6, 137.8, 138.8, 150.5, 212.9; MS *m*/*z* 285 (M^+). HRMS calcd for $C_{16}H_{15}NS_2$, 285.0646 (M^+), found 285.0642. The compound **36** did not give satisfactory elemental analysis data due to its instability.

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