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Sulfurization of Nonenolizable Diketones

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Sulfurization of nonenolizable diketones **1a–d** by Lawesson's reagent (LR) and boron trisulfide reagent (B_2S_3) was investigated. Sulfurization of 1,4-diketone **1a** with LR at 50 °C in benzene affords disulfide **2** (23%) and 1,3-dithietane **4a** (70%) as the main products, while that with B_2S_3 in refluxing toluene gives **2** (62%) as the major product. Dithietane **4a** probably arises from intramolecular head-to-tail dimerization of the initially formed 1,4-dithione **7a**, while disulfide **2** is the product of thermal rearrangement of **4a**. Sulfurization of 1,5-diketone **1b** with B_2S_3 affords 1,3-dithietane **4b** (52%) through head-to-tail dimerization of the probable intermediate, 1,5-dithione **7b**. The reaction of **1b** with LR affords a trithiaphosphorinane derivative **6**, which probably results from [2 + 2 + 2] cycloaddition of **7b** with thionophosphine sulfide **19**, which is formed by thermal dissociation of LR. **6**, when heated in refluxing toluene, undergoes cycloreversion to regenerate **19** and **7b** (**4b** as the final product in a quantitative yield), and **19** thus formed acts as a sulfurizing agent (heating benzophenone with **6** in refluxing toluene affords thiobenzophenone in 92% yield). Sulfurization of 1,6-diketone **1c** with LR affords dithione **7c** (42%), monothione **8c** (13%), 1,2,4-trithiolane **3c** (5%), and 1,3-dithietane **4c** (2%), while that with B_2S_3 gives **7c** (57%), **8c** (6%), and **4c** (20%). Sulfurization of 1,7-diketone **1d** by both reagents affords dithione **7d** and monothione **8d** in good yields. Only thiocarbonyls of **7d** do not undergo intramolecular dimerization.

The chemistry of thiocarbonyl compounds has been a matter of extensive investigation. However, most of these works have been concerned with intermolecular reactivities of thiocarbonyl groups, and studies on the intramolecular reactions between thiocarbonyls placed in the same molecule are rather limited, although it is known that thiocarbonyls, unless stabilized either sterically or electronically, are thermally labile and dimerize or trimerize in a head-to-tail fashion.[1] The most well-known example of such intramolecular interactions is the tautomerization between 1,2-dithiones and 1,2-dithietes.[2] The [3,3] sigmatropic rearrangement of divinyl disulfides to 1,4-dithiones provides another interesting example.[3] Apparently, the most currently interesting works in this field involve the intramolecular head-to-head dimerization of thiocarbonyl groups leading to 1,2-dithietanes; Steliou et al. reported that 2,2′-bis(thiobenzoyl)biphenyl, obtainable by sulfurization of the corresponding diketone, thermally affords diatomic sulfur (S_2) and 9,10-diphenylphenanthrene through the likely intermediacy of a 1,2-dithietane,[4] while Nicolaou et al. obtained the first stable 1,2-dithietane (dithiatopazine) by photochemical intramolecular dimerization of a dithionolactone.[5] Taking the background described above, especially the findings by the last two groups, into account, we have decided to investigate systematically how two thiocarbonyls placed in the same molecule interact with each other depending on the length of the carbon chain separating them. For this purpose, we have undertaken the sulfurization of a series of nonenolizable diketones.[6] Lawesson's reagent[7] and boron trisulfide reagent[8] are the sulfurization reagents of our choice. Herein we report the results of these sulfurization reactions and some properties of the resulting dithiones and related compounds.

Results

Preparation of Nonenolizable Diketones 1. 1,4-, 1,5-, 1,6-, and 1,7-diketones (**1a–d**) were chosen as the model compounds for the sulfurization and prepared in the following ways.

1,4-Diketone **1a** was prepared by reductive coupling of 2-bromoisobutyrophenone with iron pentacarbonyl in 34% yield.[9]

Dilithiation of isobutyric acid with lithium diisopropylamide (LDA) followed by addition of diiodomethane afforded 2,2,4,4-tetramethylglutaric acid in 51% yield. Treatment of this acid with phenyllithium furnished the expected 1,5-diketone **1b** in 22% yield.[10]

1,4-Dicyanobutane was exhaustively methylated with methyl iodide by use of LDA as base to give 2,5-dicyano-2,5-dimethylhexane in 62% yield.[11] The reaction of the latter nitrile with phenyllithium satisfactorily afforded 1,6-diketone **1c** in 82% yield. 1,7-Diketone **1d** was also synthesized starting from 1,5-dicyanopentane in good overall yield.

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(1) (a) Campaigne, E. *Chem. Rev.* **1946**, *39*, 1. (b) Fraser, P. S.; Robbins, L. V.; Chilton, W. S. *J. Org. Chem.* **1974**, *39*, 2509. (c) Field, L. *Synthesis* **1978**, 713. (d) Duus, F. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: New York, 1978; Vol. 3, p 373. (e) Vedejs, E.; Eberlein, T. H.; Mazur, D. J.; McClure, C. K.; Perry, D. A.; Ruggeri, R.; Schwartz, E.; Stults, J. S.; Varie, D. L.; Wilde, R. G.; Wittenberger, S. *J. Org. Chem.* **1986**, *51*, 1556 and references cited therein.

(2) (a) Köpke, B.; Voss, J. *J. Chem. Res.* (*S*) **1982**, 314. (b) Orahovatz, A.; Levinson, M. I.; Carroll, P. J.; Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1985**, *50*, 1550. See also references cited in these papers.

(3) (a) Morgenstern, J.; Mayer, R. *J. Prakt. Chem.* **1966**, *34*, 116. (b) Boelens, H.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 141. (c) Campbell, M. M.; Evgenios, D. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2866. (d) Larsson, F. C. V.; Brandsma, L.; Lawesson, S.-O. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 258. (e) Schwab, A. W.; Gilardi, R. D.; Flippen-Anderson, J. L. *Phosphorus Sulfur* **1981**, *10*, 123. (f) Tamaru, Y.; Harada, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1978**, *100*, 1923.

(4) Steliou, K.; Salama, P.; Brodeur, D.; Gareau, Y. *J. Am. Chem. Soc.* **1987**, *109*, 926.

(5) Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E.; Carroll, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 3801.

(6) Sulfurization of enolizable 1,5-dicarbonyl compounds either by H_2S/H^+ or P_4S_{10}, which principally results in the thiopyran formation, has been widely investigated. In this case however, no dithiocarbonyl compounds are involved as intermediates. For a general discussion of this reaction, see: Kuthan, J. *Adv. Heterocycl. Chem.* **1983**, *34*, 145. For application to 1,4-dithiin synthesis, see: Nakayama, J.; Motoyama, H.; Machida, H.; Shimomura, M.; Hoshino, M. *Heterocycles* **1984**, *22*, 1527.

(7) (a) Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223. (b) For a recent review, see: Cava, M. P.; Levinson, I. *Tetrahedron* **1985**, *41*, 5061.

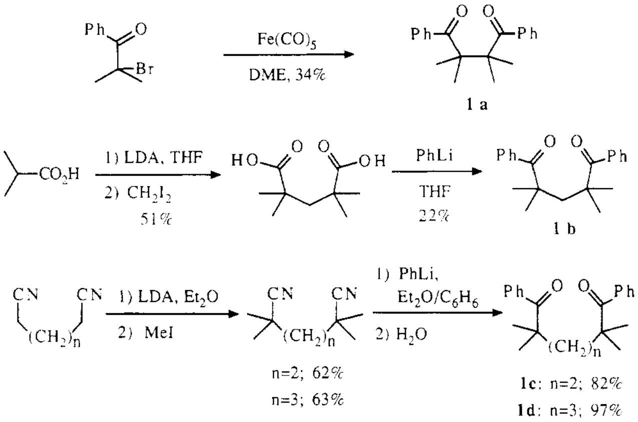
(8) Steliou, K.; Mrani, M. *J. Am. Chem. Soc.* **1982**, *104*, 3104.

(9) Alper, H.; Keung, E. C. H. *J. Org. Chem.* **1972**, *37*, 2566.

(10) Maier, G.; Roth, C.; Schmitt, R. K. *Chem. Ber.* **1985**, *118*, 704.

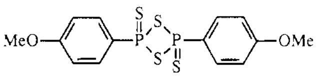
(11) Klages, C.-P.; Voss, J. *J. Chem. Res.* (*S*) **1977**, 146; *J. Chem. Res.* (*M*) **1977**, 1831.

0022-3263/90/1955-2421$02.50/0

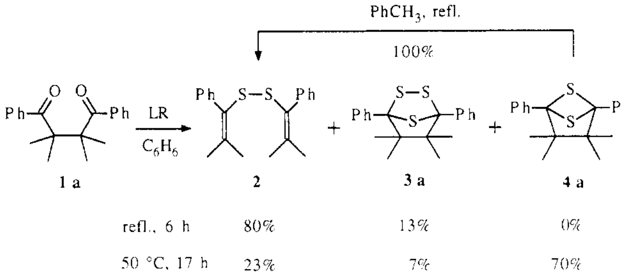


Sulfurization of Diketones with Lawesson's Reagent (LR). The sulfurization of diketones 1 was carried out with excess LR in every case, though one molecule of LR can theoretically sulfurize two carbonyls.[7]

The sulfurization of diketone **1a** proceeded easily. Heating **1a** with LR in refluxing benzene for 6 h resulted in the complete consumption of **1a**. Chromatographic workup of the mixture gave disulfide **2** (80%) and trithiolane **3a** (13%). The reaction proceeded even at 50 °C in benzene, though prolonged heating was required for the completion. In this case, the yield of **2** decreased to 23%, but instead a new product, 1,3-dithietane **4a**, was obtained in 70% yield along with a 7% yield of **3a**. ^{1}H and ^{13}C NMR spectral data of these compounds are summarized in Table I.



LR

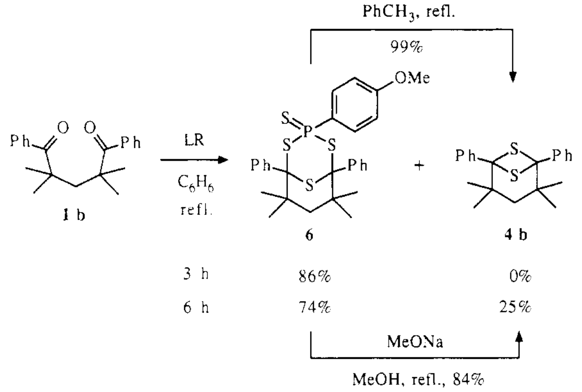


The structure of **2** was established by comparison of ^{1}H and ^{13}C NMR and mass spectral data with those of the authentic sample that was independently synthesized by sulfurization of isobutyrophenone followed by oxidation with molecular iodine.[3d] Compounds **3a** and **4a** have interesting structures in which 1,2,4-trithiolane and 1,3-dithietane rings occupy a part of bicyclic frameworks. Their structures were determined mainly by spectroscopic means. In the ^{1}H NMR spectrum of **3a** two pairs of methyls appear at δ 0.76 and 1.42 as two singlets. The ^{13}C NMR spectrum reveals that two phenyls are equivalent. The signals due to methyls appear at δ 24.7 and 26.7 and those due to two kinds of quaternary carbons at δ 56.4 and 93.4. On the other hand, the ^{1}H and ^{13}C NMR spectra of **4a** are consistent with its C_{2v} symmetrical structure in every respect.

Heating **4a** in refluxing benzene for 6 h affords **2** quantitatively. This shows that the present reaction affords initially **4a**, which then rearranges to **2** under the applied conditions. Incidentally the 1,2,4-trithiolane **3a** is stable in refluxing benzene for 6 h. However, it decomposes to give **2** as the major product when heated above its melting point.[12]

The reaction of 1,5-diketone **1b** with LR, which occurs smoothly, affords an unexpected and structurally interesting product. Heating **1b** with LR in refluxing benzene for 3 h gave a trithiaphosphorinane derivative **6** as the sole product in 86% yield.

The structure of **6** was determined by both spectroscopic means and chemical transformations. The molecular formula of **6** was determined by elemental analysis. The occurrence of the geminal methyls as two nonequivalent signals in the ^{1}H and ^{13}C NMR spectra and of the methylene protons as an AB quartet at δ 1.33 and 3.18 with J = 15 Hz in the ^{1}H NMR spectrum strongly supports the proposed structure (Table I). The ^{31}P NMR spectrum gives a single peak at δ 74.[13]



The prolonged sulfurization (6 h) of **1b** affords the 1,3-dithietane **4b** in 25% yield in addition to **6** in 74% yield. This indicates that **6** decomposes to **4b** under the conditions. Actually heating **6** alone in refluxing toluene afforded **4b** quantitatively. Further support for the structure **6** comes from the formation of **4b** in 84% yield by treatment of **6** with sodium methoxide in refluxing methanol, though the detailed mechanism of this conversion is not clear. Compound **4b** also has a C_{2v} symmetrical structure in which the 1,3-dithietane ring occupies a part of bicyclic framework, and its ^{1}H and ^{13}C NMR spectra resemble those of **4a** except for the occurrence of the signal due to the methylene (Table I).

The reaction of 1,6-diketone **1c** with LR requires higher temperatures and longer reaction times. Thus, a mixture of **1c** and LR was heated for 46 h in refluxing toluene to give dithione **7c** (42%), monothione **8c** (13%), 1,3-dithietane **4c** (2%), and 1,2,4-trithiolane **3c** (5%). Both **7c** and **8c** have a characteristic purple color of thiocarbonyl and both compounds exhibit absorption at 566 nm that is comparable to that of thiopivalophenone (556 nm)[14] in visible spectra. NMR data of these compounds are given in Table II. Noteworthy are the NMR spectra of **4c**, which differ in some respects from those of **4a** and **4b** in

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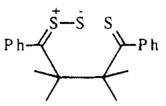
(12) The decomposition probably occurs via the cycloreversion to the thiocarbonyl S-sulfide **5**. For cycloreversion of 1,2,4-trithiolanes to thiocarbonyl S-sulfides and thiocarbonyls, see: Huisgen, R.; Rapp, J. *J. Am. Chem. Soc.* **1987**, *109*, 902.



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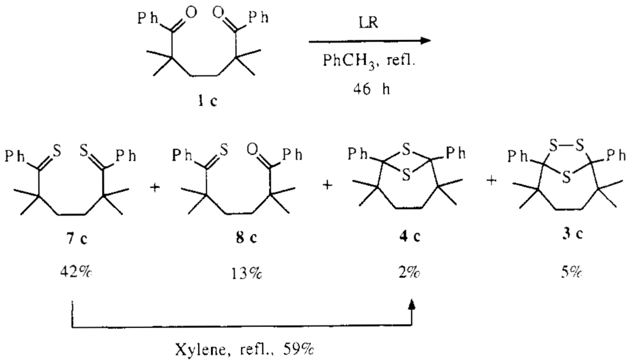
(13) Scheibye, S.; Shabana, R.; Lawesson, S.-O. *Tetrahedron* **1982**, *38*, 993.

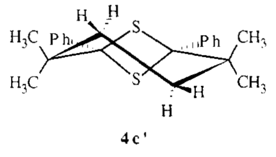
(14) Bhattacharyya, K.; Ramamurthy, V.; Das, P. K. *J. Phys. Chem.* **1987**, *91*, 5626.

Table I. ^{1}H NMR and ^{13}C NMR Spectral Data of Bicyclic Products

compd	^{1}H NMR (δ, ppm)	^{13}C NMR (δ, ppm)
3a	0.76 (s, 6 H), 1.42 (s, 6 H), 7.37–7.39 (m, 6 H), 7.59–7.61 (m, 4 H)	24.7 (q), 26.7 (q), 56.4 (s), 93.4 (s, S–C–S), 128.2 (d), 128.4 (d), 128.6 (d), 136.4 (s)
3c	0.92 (s, 6 H), 1.29 (s, 6 H), 1.78 (br t, 2 H, J = 12 Hz), 2.40 (br s, 2 H), 7.23–7.29 (m, 6 H), 7.55–7.58 (m, 4 H)	26.9 (q), 30.4 (q), 38.5 (t), 44.9 (s), 94.0 (s, S–C–S), 127.0 (d), 127.4 (d), 129.5 (d), 141.7 (s)
4a	1.37 (s, 12 H), 7.02–7.04 (m, 4 H), 7.29–7.37 (m, 6 H)	25.1 (q), 56.5 (s), 79.3 (s, S–C–S), 125.7 (d) 127.57 (d), 127.63 (d), 136.6 (s)
4b	1.24 (s, 12 H), 2.30 (s, 2 H), 6.86–7.00 (m, 4 H), 7.10–7.28 (m, 6 H)	26.8 (q), 41.9 (s), 56.0 (t), 64.7 (s, S–C–S), 125.3 (d), 126.7 (d), 127.2 (d), 141.4 (s)
4c	0.64 (br s, 6 H), 1.23 (br s, 6 H), 1.63 (br d, 2 H, J = 13 Hz), 2.94 (br d, 2 H, J = 13 Hz), 6.91 (d, 4 H, J = 7 Hz), 7.11 (t, 2 H, J = 7 Hz), 7.20 (t, 4 H, J = 7 Hz)	21.0 (q), 26.7 (q), 39.6 (t), 42.6 (s), 55.3 (s, S–C–S), 125.8 (d), 126.1 (d), 126.7 (d), 144.7 (s)
6	0.92 (s, 6 H), 1.23 (s, 6 H), 1.33 (d, 1 H, J = 15 Hz), 3.18 (d, 1 H, J = 15 Hz), 3.61 (s, 3 H, OCH_3), 6.46–6.50 (m, 2 H), 7.25–7.38 (m, 8 H), 7.81 (d, 4 H, J = 8 Hz)	26.8 (q), 27.9 (q), 43.2 (s), 49.4 (dd, CH_2), 55.2 (q, OCH_3), 75.5 [d, J_{PC} = 6 Hz, (d), S–C–S], 113.8 [d, J_{PC} = 17 Hz, (dd)], 127.6 (d), 128.2 (d), 128.3 (d), 130.6 [d, J_{PC} = 15 Hz, (dd)], 133.3 [d, J_{PC} = 99 Hz, (d)], 140.4 (s), 161.4 [d, J_{PC} = 3.5 Hz, (d)]

spite of its apparent C_{2v} symmetrical structure (Table I). The geminal methyls of **4c** appear as two nonequivalent rather broad singlets at δ 0.64 and 1.23 and the methylene protons as two doublets at δ 1.63 and 2.94 with J = 13 Hz in the ^{1}H NMR spectrum. Meanwhile, the two quaternary carbons carrying methyls and the two methylene carbons are each equivalent and resonate at δ 42.6 and 39.6, respectively, in the ^{13}C NMR spectrum. These observations reveal that **4c** exists in a conformation such as **4c′** in solutions around room temperature.[15] The free energy of activation ($\Delta G^{\ddagger}$) of the ring inversion of **4c′** is estimated by the coalescence temperature method. In the ^{1}H NMR (400 MHz) spectrum the two geminal protons of **4c** coalesced at 89 °C in DMSO-d_6, while the two geminal methyls coalesced at 77 °C. Thus, the calculated $\Delta G^{\ddagger}$ value at 362 K is 16.9 kcal/mol. The trithiolane **3c** shows an NMR pattern similar to that of **3a** (Table I.)

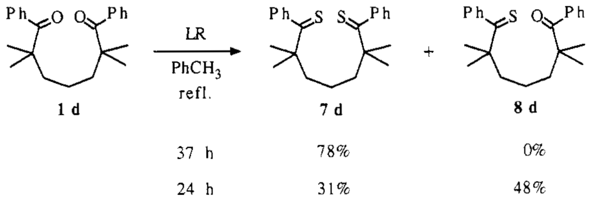




4c′

1,3-Dithietane **4c** is probably formed from **7c** by intramolecular head-to-tail dimerization. Actually, heating **7c** in boiling xylene for 61 h gave **4c** in 59% yield. When **7c** was heated with LR in refluxing xylene, trithiolane **3c** was obtained in 28% yield along with **4c** in 16% yield. Therefore **3c** must be formed by reaction of **7c** with sulfur provided from LR. The formation of a 1,2,4-trithiolane derivative by reaction of cyclohexanethione with activated sulfur has been already reported.[3a]

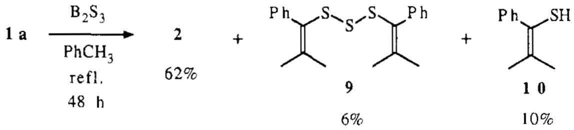
The reaction of 1,7-diketone **1d** with LR in refluxing toluene for 37 h afforded 1,7-dithione **7d** in 78% yield. In this case, neither the 1,3-dithietane nor the 1,2,4-trithiolane derivative was formed. Dithione **7d** does not show a tendency to undergo intramolecular dimerization leading to the corresponding 1,3-dithietane. When the reaction was quenched after 24 h, monothione **8d** was obtained in 48% yield along with **7d** in 31% yield. NMR data of **7d** and **8d** are given in Table II.



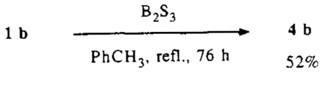
Sulfurization of Diketones with Boron Trisulfide Reagent. Boron trisulfide reagent (B_2S_3) prepared in situ from bis(trimethylsilyl) sulfide and boron trichloride[8] was used in excess for sulfurization.

The sulfurization of 1,4- and 1,5-diketones (**1a** and **1b**) with B_2S_3 required higher temperatures and longer reaction times compared to those with LR, although sulfurization of 1,6- and 1,7-diketones (**1c** and **1d**) proceeded at a comparable rate with both reagents.

Thus toluene was used instead of benzene as the solvent for sulfurization of **1a**, and the mixture was refluxed as long as 48 h. The resulting products are disulfide **2** (62%), trisulfide **9** (6%), and enethiol **10** (10%). Disulfide **2** must be formed from dithietane **4a** as already described, though the latter compounds could not be isolated in the present case. Disulfide **2** affords a 3:2 mixture of **2** and **9** when heated with elemental sulfur in refluxing toluene. Therefore **9** must be formed from **2** and sulfur which exists in the system as a contaminant. The enethiol **10** would be formed by reduction of disulfide **2**, though the species acting as reducing agent is not clear.



The reaction of 1,5-diketone **1b** with B_2S_3 is also sluggish in refluxing toluene and required 76 h for completion. The reaction is clean, however, and afforded 1,3-dithietane **4b** as the sole product in 52% yield.



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[15] Molecular model analysis shows that 4c′ is the least sterically hindered and most stable conformer. For a general discussion of the conformation of heteroatom-containing seven-membered rings, see: Armarego, W. L. F. In *Stereochemistry of Heterocyclic Compounds*; Wiley: New York, 1976.

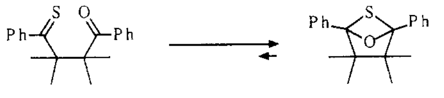
Sulfurization of diketones **1c** and **1d** with B_2S_3 also requires prolonged heating. The reaction of **1c** with B_2S_3 in refluxing toluene for 48 h afforded dithione **7c** (57%) as the main product in addition to monothione **8c** (6%) and dithietane **4c** (20%). On the other hand, diketone **1d** afforded dithione **7d** (76%) and monothione **8d** (6%) on being heated with B_2S_3 in refluxing toluene for 48 h.

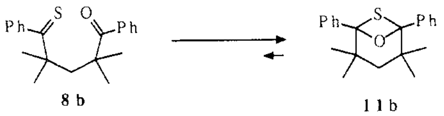
$$\mathbf{1c} \xrightarrow[\text{PhCH}_3,\ \text{refl.}\ 48\ \text{h}]{B_2S_3} \mathbf{7c}\ (57\%) + \mathbf{8c}\ (6\%) + \mathbf{4c}\ (20\%)$$

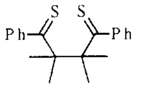
$$\mathbf{1d} \xrightarrow[\text{PhCH}_3,\ \text{refl.}\ 48\ \text{h}]{B_2S_3} \mathbf{7d}\ (76\%) + \mathbf{8d}\ (6\%)$$

Discussion

The first things that we must discuss are the following observations. In the sulfurization of **1c** and **1d**, the purple color due to monothiones **8c** and **8d** develops during the reaction, though the color due to dithiones **7c** and **7d** finally prevails. Meanwhile, in the case of **1a** and **1b**, the color of the mixture does not change markedly during the reaction. A tentative explanation for this phenomenon is given below. Monothiones **8a** and **8b**, once formed, immediately undergo intramolecular head-to-tail dimerization to give oxathietanes **11a** and **11b**, respectively, which are thought to be colorless.[16] Sulfurization of the remaining second carbonyl group would be attained via the equilibrium between **8a** and **11a** (**8b** and **11b**), though it lies far to the right and the concentration of **8a** (**8b**) is kept very low at the stationary state. Finally, the resulting dithiones **7a** and **7b** must be immediately converted to the colorless products.







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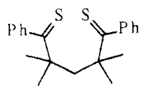
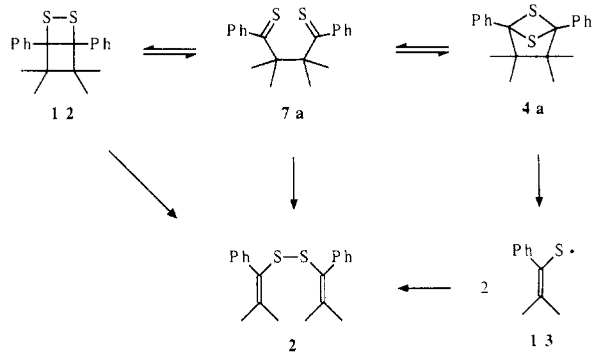


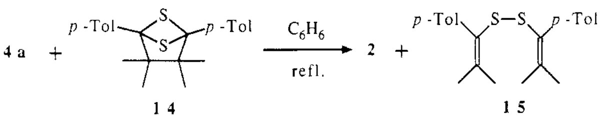
7 b

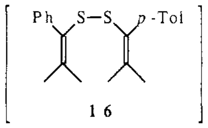
Sulfurization of **1a** and **1b** with LR is curious. Only these two reactions proceed more readily as compared to the other cases. Obviously in the other cases the sulfurization of two carbonyls occurs independently in a stepwise manner because monothiones **8c** and **8d** are isolable. In the above two cases, a special mechanism that accelerates the sulfurization may be operative.

Apart from the difference of the sulfurization mechanism, **1a** would be ultimately converted to 1,4-dithione **7a** by both reagents. Then **7a** undergoes intramolecular head-to-tail dimerization to give 1,3-dithietane **4a**.

As to the rearrangement of **4a** to disulfide **2**, there exist three plausible mechanisms. The first mechanism involves the [3,3] sigmatropic rearrangement of dithione **7a**, which is in thermal equilibrium with **4a**. This is the reverse process of the known rearrangement of divinyl disulfides to 1,4-dithiones.[3] The second mechanism also involves **7a** as an intermediate which undergoes head-to-head dimerization to give 1,2-dithietane **12**. This is the very process that we expected to occur at the beginning of the present study. Then **12** undergoes ring opening to give **2** but not decomposition to give diatomic sulfur (S_2) and the corresponding cyclobutene because the former process allows much more relief from the strains. The last mechanism involves thermal dissociation of **4a** into two resonance-stabilized thiyl radicals **13** and their recombination, although it must require higher activation energy for the carbon–carbon bond cleavage and hence seems to be less probable (the rearrangement of **4a** to **2** is not affected by the presence of molecular oxygen). Actually, heating of the mixture of **4a** and its *p*-tolyl derivative **14** afforded isomerized disulfides **2** and **15** without the formation of a mixed disulfide **16**.







Sulfurization of **1b** with B_2S_3 would produce 1,5-dithione **7b**, which undergoes head-to-tail dimerization to give dithietane **4b**. The isolable 1,6-dithione **7c** also undergoes head-to-tail dimerization to afford **4c**. In both cases, no 1,2-dithietane formation, head-to-head dimerization, was observed. This implies that 1,2-dithietane formation is an energetically unfavorable process compared to 1,3-dithietane formation probably because of the destabilizing repulsion between the lone pairs of electrons on the adjacent sulfur atoms imposed by the geometrical constraints of the former four-membered ring.[5] Therefore, for synthesizing 1,2-dithietanes, more rigid conformational or electronic constraints that completely suppress 1,3-dithietane formation would be strongly required. The successful isolation of dithiones **7c** and **7d** is due to the fact that the dimerization of these compounds leads to the bicyclic systems containing medium-size rings.

We finally discuss the mechanism of the formation of trithiaphosphorinane derivative **6** from **1b** and LR and some interesting properties of **6** and related compounds. The formation of trithiaphosphorinane derivatives by reaction of ketones with LR is precedented; cyclopentanone

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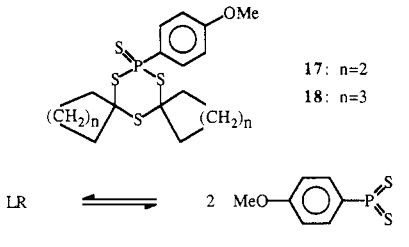
[16] To our knowledge, only two reports have appeared on this ring system. The patent work describes the preparation of (±)-(*cis*-4-methyl-1,3-oxathietan-2-yl)phosphonic acid *S*,*S*-dioxide: Firestone, R. A. Ger. Offen. 1,924,138; *Chem. Abstr.* **1970**, *72*, 111613h. The theoretical work discusses through-space and through-bond interactions between heteroatoms in the parent 1,3-oxathietane: Pasto, D. J.; Chipman, D. M.; Worman, J. J. *J. Phys. Chem.* **1982**, *86*, 3981.

Table II. ^{1}H NMR and ^{13}C NMR Spectral Data of 1,ω-Diketones, 1-Oxo-ω-thiones, and 1,ω-Dithiones

compd	^{1}H NMR (δ, ppm)	^{13}C NMR (δ, ppm)
1c	1.22 (s, 12 H), 1.70 (s, 4 H), 7.27–7.68 (m, 10 H)	25.7 (q), 35.5 (t), 46.9 (s), 127.3 (d), 127.7 (d), 130.5 (d), 138.3 (s), 207.3 (s, C=S)
1d	1.31–1.21 (m, 2 H), 1.24 (s, 12 H), 1.63–1.67 (m, 4 H), 7.33–7.46 (m, 6 H), 7.54–7.59 (m, 4 H)	20.2 (t), 26.0 (q), 41.3 (t), 47.8 (s), 127.4 (d), 128.1 (d), 130.7 (d), 139.1 (s), 208.8 (s, C=S)
8c	1.26 (s, 6 H), 1.30 (s, 6 H), 1.75 (s, 4 H), 7.13–7.70 (m, 10 H)	26.1 (q), 29.4 (q), 35.7 (t), 37.9 (t), 47.4 (s), 54.8 (s), 124.3 (d), 127.5 (d), 127.6 (d), 128.1 (d), 128.4 (d), 130.9 (d), 138.9 (s), 151.3 (s), 208.3 (s, C=O), 264.2 (s, C=S)
8d	1.15–1.25 (m, 2 H), 1.28 (s, 6 H), 1.31 (s, 6 H), 1.63–1.73 (m, 4 H), 7.05–7.08 (m, 2 H), 7.21–7.31 (m, 3 H), 7.36–7.47 (m, 3 H), 7.60–7.63 (m 2 H)	20.2 (t), 26.2 (q), 29.1 (q), 41.4 (t), 43.2 (t), 47.8 (s), 55.3 (s), 124.6 (d), 127.4 (d), 127.5 (d), 128.07 (d), 128.11 (d), 130.8 (d), 139.0 (s), 151.3 (s), 209.0 (s, C=O), 265.0 (s, C=S)
7c	1.31 (s, 12 H), 1.81 (s, 4 H), 7.08–7.31 (br s, 10 H)	29.4 (q), 37.9 (t), 54.8 (s), 124.8 (d), 127.3 (d), 128.2 (d), 151.2 (s), 264.2 (s, C=S)
7d	1.23–1.32 (m, 2 H), 1.37 (s, 12 H), 1.72–1.77 (m, 4 H), 7.16 (d, 4 H, J = 7 Hz), 7.24–7.34 (m, 6 H)	20.1 (t), 29.2 (q), 43.3 (t), 55.3 (s), 124.7 (d), 127.3 (d), 128.1 (d), 151.3 (s), 264.8 (s, C=S)

and cyclohexanone react with LR to give **17** and **18**, respectively.[13] LR is known to thermally dissociate into two molecules of the thionophosphine sulfide **19**, which acts as the actual species of sulfurization.[13] The simplest explanation for the formation of **6** involves the [2 + 2 + 2] cycloaddition of dithione **7b** with **19**, which probably occurs in a stepwise manner via a 1,4-dipolar intermediate.[17,18] The concerted mechanism that requires termolecular collisions is unlikely at least in the formation of **17** and **18**.



17: n=2

18: n=3

19

The formation of 1,3-dithietane **4b** by thermolysis of **6** indicates that **6** undergoes [2 + 2 + 2] cycloreversion to **7b** (**4b** as the product) and **19**. If this is the case, **6** should act as the sulfurization agent. Actually, heating a mixture of **6** and benzophenone in refluxing toluene afforded thiobenzophenone in 92% yield (calculated from UV–vis spectral intensities[19]) along with a quantitative yield of **4b**. In order to know the generality of this sulfurization, compound **17** was allowed to react with benzophenone in refluxing toluene, which furnished thiobenzophenone in 68% yield. Therefore, this type of trithiaphosphorinane derivative is capable of acting as a new sulfurization agent.

Experimental Section

General. Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H NMR spectra were measured at 400 or 90 MHz and ^{13}C NMR spectra were measured at 100.6 or 22.49 MHz using $CDCl_3$ as the solvent. ^{31}P NMR spectra were obtained at 36.28 MHz using phosphoric acid as an external standard and $CDCl_3$ as the solvent. Low- and high-resolution mass spectra were measured at 70 eV in the EI mode. Dry column chromatography was performed with a 1:5 mixture of Merck Kieselgel 60 F_{254} (70–230 mesh) and Merck Kieselgel 60 (70–230 mesh) packed in a seamless cellulose tubing and visualized with a 254-nm UV lamp. Analytical HPLC was performed with a Du Pont Zorbax ODS 4.6 mm × 15 cm column using methanol. Solutions were dried with anhydrous $MgSO_4$. Elemental analyses were performed by the Analytical Center of Saitama University, for which we thank Professor M. Sato, Mr. M. Kubo, and Mrs. E. Morikubo. Lawesson's reagent (LR) was prepared from anisole and phosphorus pentasulfide.[7a] Bis(trimethylsilyl) sulfide (Fluka) and BCl_3 (Wako) were used as purchased for the preparation of B_2S_3 reagent.[8]

Preparation of Diketones 1. 2,2,3,3-Tetramethyl-1,4-diphenylbutane-1,4-dione (1a)[9] and 2,2,4,4-tetramethyl-1,5-diphenylpentane-1,5-dione (1b)[10] were prepared according to the literature method.

2,2,5,5-Tetramethyl-1,6-diphenylhexane-1,6-dione (1c). Phenyllithium was prepared from bromobenzene (4.70 g, 30 mmol) and lithium (0.42 g, 60 mmol) in ether (30 mL). To this phenyllithium solution a solution of 2,5-dicyano-2,5-dimethylhexane[11] (0.48 g, 2.9 mmol) in benzene (30 mL) was added dropwise at 0 °C. After stirring for 1.5 h at this temperature, the reaction was quenched by adding 3 mL of MeOH to the mixture. The resulting mixture was washed with water, dried, and evaporated under reduced pressure. The resulting yellow solid was purified by dry column chromatography (silica gel, CH_2Cl_2) and then by recrystallization from hexane to give 0.77 g (82%) of **1c** as colorless crystals: mp 81–81.5 °C; MS m/z 322 (M^+); for ^{1}H and ^{13}C NMR spectra, see Table II. Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 82.04; H, 8.31.

2,2,6,6-Tetramethyl-1,7-diphenylheptane-1,7-dione (1d). A solution of 2,6-dicyano-2,6-dimethylheptane[11] (4.87 g, 27 mmol) in benzene (80 mL) was added to a solution of phenyllithium prepared from bromobenzene (19.3 g, 123 mmol) and lithium (1.71 g, 246 mmol) in ether (40 mL). The mixture was stirred at 0 °C for 3 h and then at ambient temperature for 3 h. To this mixture was added 3 mL of MeOH followed by a mixture of MeOH (3 mL) and water (20 mL). After being stirred for 1 h, the mixture was extracted with CH_2Cl_2. The extracts were washed with water, dried, and evaporated to leave a yellow oil. Chromatographic purification on a dry silica gel column (CH_2Cl_2) of the oil gave 9.12 g (97%) of **1d**: colorless crystals, mp 49–50 °C (hexane); MS m/z 336 (M^+); for ^{1}H and ^{13}C NMR spectra, see Table II. Anal. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 81.87; H, 8.43.

Sulfurization of 1,4-Dione 1a with LR. (I) In Refluxing Benzene. A mixture of **1a** (147 mg, 0.5 mmol) and LR (607 mg, 1.5 mmol) in benzene (5 mL) was refluxed under N_2 for 6 h. The initial pale yellow mixture turned brown after 0.5 h and then colorless after 1 h. The reaction mixture was cooled to room temperature and the solvent was removed. The residue was subjected to dry column chromatography (silica gel, 1:1 CH_2Cl_2–hexane) to afford 130 mg (80%) of bis(2-methyl-1-phenyl-1-propenyl) disulfide (**2**) and 22 mg (13%) of 2,2,3,3-tetramethyl-1,4-diphenyl-5,6,7-trithiabicyclo[2.2.1]heptane (**3a**). Spectroscopic data of **2** agreed with those of an authentic sample prepared independently (vide infra). **3a**: colorless crystals, mp 223–224 °C dec; MS m/z (relative intensity) 358 (M^+, 5), 294 ($M^+ - 2S$, 100), 279 (53). ^{1}H and ^{13}C NMR data of **3a** are listed in Table I. Anal. Calcd for $C_{20}H_{22}S_3$: C, 66.99; H, 6.18; S, 26.82. Found: C, 66.76; H, 6.10; S, 26.74.

(II) At 50 °C. A mixture of **1a** (147 mg, 0.5 mmol) and LR (607 mg, 1.5 mmol) in benzene (5 mL) was heated for 17 h at 50 °C. The colorless mixture was cooled to room temperature and the resulting precipitates were filtered. The filtrate was evaporated to give a dark green solid, which was subjected to dry column chromatography (silica gel, 1:1 CH_2Cl_2–hexane) to yield 38 mg (23%) of **2** and 127 mg of a mixture of **3a** and 2,2,3,3-tetramethyl-1,4-diphenyl-5,6-dithiabicyclo[2.1.1]hexane (**4a**). The yields of **3a** and **4a** were determined by ^{1}H NMR to be 7 and 70%,

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(17) Gilchrist, T. L.; Storr, R. C. In *Organic Reactions and Orbital Symmetry*; Cambridge University Press: London, 1972; p 129.

(18) It is known that **16** acts as a dienophile; see refs 7b and 13.

(19) Lees, W. A.; Burawoy, A. *Tetrahedron* **1964**, *20*, 1527.

respectively. Pure **4a** was obtained by repeated recrystallization of the mixture from EtOH. **4a**: colorless plates, mp 134–134.5 °C; MS *m/z* (relative intensity) 326 (M^+, 67), 163 (100), 129 (78). ^1H and ^{13}C NMR data of **4a** are shown in Table I. Anal. Calcd for $C_{20}H_{22}S_2$: C, 73.57; H, 6.79; S, 19.64. Found: C, 73.39; H, 6.78; S, 19.74.

Independent Synthesis of Disulfide 2. A mixture of isobutyrophenone (2.23 g, 15 mmol) and LR (6.06 g, 15 mmol) in benzene (30 mL) was refluxed for 2 days. The mixture was cooled and the precipitates were removed by filtration. The filtrate was washed with aqueous $NaHCO_3$ twice and dried. Evaporation of the solvent followed by Kugelrohr distillation (130–150 °C/20 mmHg) yielded a 2:1 mixture of 2-methyl-1-phenyl-1-propenethiol (**10**) and the starting ketone as a purple liquid (1.0 g). The mixture was dissolved in 20 mL of MeOH containing ca. 0.2 g of KOH. To this solution, I_2 was added in small portions until it was consumed no longer. Aqueous $Na_2S_2O_3$ was added to the dark brown mixture to remove excess iodine, and the resulting mixture was extracted with CH_2Cl_2. The organic layer was washed with water and dried. The oily residue obtained by removal of the solvent was subjected to dry column chromatography (silica gel, hexane) to yield 547 mg (11%, based on isobutyrophenone) of **2** as a yellow oil: ^1H NMR δ 1.58 (s, 6 H), 1.81 (s, 6 H), 7.12–7.31 (m, 10 H); ^{13}C NMR δ 22.6 (q), 23.2 (q), 126.6 (d), 127.6 (d), 130.3 (d), 130.9 (s), 137.5 (s), 139.9 (s); MS *m/z* (relative intensity) 326 (M^+, 100), 163 (85), 129 (98).

Thermal Isomerization of 1,3-Dithietane 4a to Disulfide 2. A solution of **4a** (65 mg, 0.2 mmol) in benzene (5 mL) was refluxed under N_2 for 6 h and cooled to room temperature. Removal of the solvent left a yellow oil, the ^1H NMR spectrum of which revealed the quantitative formation of **2**.

Sulfurization of 1,5-Dione 1b with LR. (I) In Refluxing Benzene for 3 h. A mixture of **1b** (154 mg, 0.5 mmol) and LR (485 mg, 1.2 mmol) in benzene (10 mL) was refluxed for 3 h. The reaction mixture was filtered to remove the resulting precipitates, and the filtrate was washed successively with aqueous $NaHCO_3$ and 2 M KOH and dried. After removal of the solvent, the residual solid was purified by dry column chromatography (silica gel, 3:1 hexane–ether) to yield 235 mg (86%) of 7-(4-methoxyphenyl)-2,2,4,4-tetramethyl-1,5-diphenyl-7-phospha-6,8,9-trithiabicyclo[3.3.1]nonane 7-sulfide (**6**): colorless crystals; MS *m/z* (relative intensity) 340 ($M^+ - MeOC_6H_4PS_2$, 8), 308 (8), 219 (100), 121 (40). This compound does not show a clear melting point, decomposing at 161–202 °C. ^1H and ^{13}C NMR data are shown in Table I. Anal. Calcd for $C_{28}H_{31}OPS_4$: C, 61.96; H, 5.76. Found: C, 61.73; H, 5.95.

(II) In Refluxing Benzene for 6 h. A mixture of **1b** (154 mg, 0.5 mmol) and LR (607 mg, 1.5 mmol) in benzene (5 mL) was refluxed for 6 h. A workup similar to that described above gave 202 mg (74%) of **6** and 42 mg (25%) of 2,2,4,4-tetramethyl-1,5-diphenyl-6,7-dithiabicyclo[3.1.1]heptane (**4b**): colorless crystals, mp 226–227 °C (cyclohexane); MS *m/z* (relative intensity) 340 (M^+, 8), 219 (100), 162 (24), 121 (55). ^1H and ^{13}C NMR data are listed in Table I. Anal. Calcd for $C_{21}H_{24}S_2$: C, 74.07; H, 7.10; S, 18.83. Found: C, 74.23; H, 7.09; S, 19.04.

Conversion of Trithiaphosphorinane Derivative 6 to 1,3-Dithietane 4b. (I) Thermolysis. A solution of **6** (109 mg, 0.2 mmol) in toluene (3 mL) was refluxed for 4 h. The resulting mixture was washed successively with aqueous Na_2CO_3 and water and dried. Removal of the solvent followed by chromatographic purification on a dry silica gel column (1:1 CH_2Cl_2–hexane) yielded 68 mg (99%) of **4b**.

(II) MeONa-Induced Methanolysis. Sodium methoxide (44 mg, 0.8 mmol) was added to a stirring solution of **6** (201 mg, 0.37 mmol) in MeOH (10 mL). The mixture was refluxed for 20 h and cooled to room temperature. Water and CH_2Cl_2 were added to the mixture. The organic layer was separated, washed with water, and dried. Removal of the solvent gave 106 mg (84%) of nearly pure **4b**.

Sulfurization of 1,6-Dione 1c with LR. A mixture of **1c** (161 mg, 0.5 mmol) and LR (1.01 g, 2.5 mmol) in toluene (10 mL) was refluxed under N_2 for 46 h. The resulting mixture was evaporated and the residue was subjected to dry column chromatography (silica gel, 1:1 CH_2Cl_2–hexane). The first fraction contained 14 mg of a mixture of **3c** and **4c**. Separation of the above mixture cannot be attained by chromatographic means. However, **4c** is obtained in a pure form by thermal isomerization of **7c** as described below. This makes it possible to identify the signals due to **3c** in the ^1H and ^{13}C NMR spectra of the mixture. Furthermore, the mass spectrum of the mixture afforded the parent peak corresponding to the structure **3c**. The yields of **3c** and **4c** were estimated to be 5 and 2%, respectively, by ^1H NMR analysis. The second fraction gave 2,2,5,5-tetramethyl-1,6-diphenylhexane-1,6-dithione (**7c**) (75 mg, 42%) and the last one 2,2,5,5-tetramethyl-1-oxo-1,6-diphenylhexane-6-thione (**8c**) (23 mg, 13%). ^1H and ^{13}C NMR data of **3c**, **4c**, **7c**, and **8c** are listed in Tables I and II. **3c**: MS *m/z* (relative intensity) 386 (M^+, 30), 322 ($M^+ - 2S$, 100). **7c**: purple crystals, mp 74.0–74.5 °C (hexane); visible spectrum (hexane) 566 nm (ϵ = 277); MS *m/z* (relative intensity) 354 (M^+, 31), 321 (7), 290 (14), 233 (100), 121 (73). Anal. Calcd for $C_{22}H_{26}S_2$: C, 74.52; H, 7.39. Found: C, 74.25; H, 7.55. **8c**: purple crystals, mp 91–91.5 °C (hexane); visible spectrum (hexane) 566 nm (ϵ = 115); MS *m/z* (relative intensity) 338 (M^+, 58), 305 (55), 233 (16), 217 (72), 121 (84), 105 (100). Anal. Calcd for $C_{22}H_{26}OS$: C, 78.06; H, 7.74. Found: C, 77.50; H, 8.06.

Thermal Isomerization of 1,6-Dithione 7c to 1,3-Dithietane 4c. A solution of **7c** (135 mg, 0.38 mmol) in xylene (15 mL) was refluxed under N_2 for 61 h. The xylene was removed under reduced pressure and the residue was purified by dry column chromatography (silica gel, 1:1 CH_2Cl_2–hexane) to give 74 mg (59%) of **4c** in addition to 13 mg (10%) of the starting material and 12 mg (10%) of **8c**. **4c**: colorless plates, mp 224.5–226 °C (hexane); MS *m/z* (relative intensity) 354 (M^+, 29), 233 (100), 121 (57). Anal. Calcd for $C_{22}H_{26}S_2$: C, 74.52; H, 7.39. Found: C, 74.30; H, 7.66.

Reaction of 1,6-Dithione 7c with LR. A mixture of **7c** (101 mg, 0.285 mmol) and LR (576 mg, 1.43 mmol) in xylene (10 mL) was refluxed under N_2 for 44 h. The solvent was removed under reduced pressure and the residue was subjected to dry column chromatography (silica gel, 1:1 CH_2Cl_2–hexane) to give 47 mg of a mixture of **3c** (28%) and **4c** (16%) in addition to 33 mg (33%) of **7c**.

Sulfurization of 1,7-Dione 1d with LR. A mixture of **1d** (168 mg, 0.5 mmol) and LR (607 mg, 1.5 mmol) in toluene (10 mL) was refluxed under N_2 for 24 h. The resulting precipitates were filtered and the filtrate was concentrated to dryness. The residue was subjected to dry column chromatography (silica gel, 1:1 CH_2Cl_2–hexane) to afford 57 mg (31%) of 2,2,6,6-tetramethyl-1,7-diphenylheptane-1,7-dithione (**7d**) and 85 mg (48%) of 2,2,6,6-tetramethyl-1-oxo-1,7-diphenylheptane-7-thione (**8d**). **7d**: purple oil; visible spectrum (hexane) 565 nm (ϵ = 228); MS *m/z* 368 (M^+). HRMS calcd for $C_{23}H_{28}S_2$ *m/z* 368.1633, found 368.1680. **8d**: purple oil; visible spectrum (hexane) 565 nm (ϵ = 80); MS *m/z* 352 (M^+). HRMS calcd for $C_{23}H_{28}OS$ *m/z* 352.1861, found 352.1879. ^1H and ^{13}C NMR data of **7d** and **8d** are summarized in Table II.

Sulfurization of 1,4-Dione 1a with B_2S_3. To a solution of **1a** (147 mg, 0.5 mmol) in toluene (10 mL) were added bis(trimethylsilyl) sulfide (890 mg, 5 mmol) and BCl_3 (390 mg, 3.3 mmol) successively with syringes through a rubber septum under N_2. The mixture was refluxed for 48 h and cooled to room temperature. To the resulting reaction mixture were added water and benzene. The organic layer was separated, washed with water, and dried. After removal of the solvent, the residue was subjected to dry column chromatography (silica gel, hexane) to give 17 mg (10%) of 2-methyl-1-phenyl-1-propenethiol (**10**) and 110 mg of a mixture of **2** and bis(2-methyl-1-phenyl-1-propenyl) trisulfide (**9**). The yields of **2** and **9** were estimated as 62 and 6%, respectively, by ^1H NMR analysis. **9**: ^1H NMR δ 1.73 (s, 6 H), 2.07 (s, 6 H), 7.0–7.5 (m, 10 H); MS *m/z* 358 (M^+).

Reaction of Disulfide 2 with Sulfur. Disulfide **2** (113 mg, 0.345 mmol) and elemental sulfur (11 mg, 0.35 mmol) were dissolved in xylene (5 mL). The solution was heated under reflux for 8 h. After removal of the solvent, the resulting orange residue was subjected to dry column chromatography (silica gel, hexane) to give a yellow oil (107 mg), which was revealed to be a mixture of **2** and **9** in a ratio of ca. 3:2 by ^1H NMR analysis.

Sulfurization of 1,5-Dione 1b with B_2S_3. To a solution of **1b** (93 mg, 0.3 mmol) in toluene (10 mL) were successively added bis(trimethylsilyl) sulfide (118 mg, 0.66 mmol) and BCl_3 (52 mg, 0.44 mmol) by syringes through a rubber septum under N_2. The mixture was heated under reflux for 50 h. At this point, a part of the starting material still remained unchanged (TLC), and thus bis(trimethylsilyl) sulfide (420 mg, 2.3 mmol) and BCl_3 (180 mg, 1.6 mmol) were added further and the mixture was refluxed for an additional 26 h. To the resulting mixture were added water and benzene. The organic layer was separated, washed with water, and dried. Removal of the solvent followed by purification with dry column chromatography (silica gel, 1:1 CH_2Cl_2–hexane) gave 53 mg (52%) of **4b**.

Sulfurization of 1,6-Dione 1c with B_2S_3. To a solution of **1c** (161 mg, 0.5 mmol) in toluene (25 mL) were successively added bis(trimethylsilyl) sulfide (890 mg, 5 mmol) and BCl_3 (390 mg, 3.3 mmol) by syringes through a rubber septum under N_2. The mixture was refluxed for 48 h and then the solvent was removed under reduced pressure. The residue was subjected to dry column chromatography (silica gel, 1:1 CH_2Cl_2–hexane) to give 35 mg (20%) of **4c**, 100 mg (57%) of **7c**, and 10 mg (6%) of **8c**.

Sulfurization of 1,7-Dione 1d with B_2S_3. To a solution of **1d** (181 mg, 0.5 mmol) in toluene (20 mL) were successively added bis(trimethylsilyl) sulfide (890 mg, 5 mmol) and BCl_3 (390 mg, 3.3 mmol) by syringes through a rubber septum under N_2. The mixture was heated under reflux for 48 h and the solvent was removed. The residue was purified by dry column chromatography (silica gel, 1:1 CH_2Cl_2–hexane) to provide 140 mg (76%) of **7d** and 11 mg (6%) of **8d**.

Preparation of 2,2,3,3-Tetramethyl-1,4-bis(4-methylphenyl)-5,6-dithiabicyclo[2.1.1]hexane (14). 2,2,3,3-Tetramethyl-1,4-bis(4-methylphenyl)butane-1,4-dione (**20**) was prepared by a method similar to that used for **1a**.[9] A solution of **20** (136 mg, 0.422 mmol) and LR (512 mg, 1.27 mmol) in benzene (10 mL) was heated for 5 h at 51–54 °C. The mixture was cooled to room temperature and the solvent was removed. The residue was subjected to dry column chromatography (silica gel, 1:1 CH_2Cl_2–hexane) to afford 16 mg (11%) of bis[2-methyl-1-(4-methylphenyl)-1-propenyl] disulfide (**15**) and 115 mg of an inseparable mixture of **14** and 2,2,3,3-tetramethyl-1,4-bis(4-methylphenyl)-5,6,7-trithiabicyclo[2.2.1]heptane (**21**). The yield of **14** and **21** were determined by ^{1}H NMR to be 53 and 22%, respectively. The mixture obtained above was used in the isomerization experiment. **20**: colorless crystals, mp 106.0–106.5 °C; ^{1}H NMR δ 1.41 (s, 12 H), 2.36 (s, 6 H), 7.17 (d, J = 8 Hz, 4 H), 7.50 (d, J = 8 Hz, 4 H); ^{13}C NMR δ 20.6 (q), 23.9 (q), 53.7 (s), 127.1 (d), 128.1 (d), 138.2 (s), 139.4 (s), 210.9 (s); MS m/z 322 (M^+). Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.79; H, 8.02. **15**: colorless crystals, mp 111–112 °C: ^{1}H NMR δ 1.60 (s, 6 H), 1.81 (s, 6 H), 2.36 (s, 6 H), 7.02 (d, J = 8 Hz, 4 H), 7.13 (d, J = 8 Hz, 4 H); ^{13}C NMR δ 21.3 (q), 22.9 (q), 23.3 (q), 128.3 (d), 130.3 (d), 130.9 (s), 136.2 (s), 137.1 (s), 137.3 (s); MS m/z (relative intensity) 354 (M^+, 40), 177 (80), 145 (100). HRMS calcd for $C_{22}H_{26}S_2$ m/z 354.1476, found 354.1428. **14**: ^{1}H NMR δ 1.34 (s, 12 H), 2.32 (s, 6 H), 6.90 (d, J = 8 Hz, 4 H), 7.11 (d, J = 8 Hz, 4 H); ^{13}C NMR δ 21.2 (q), 25.1 (q), 56.3 (s), 79.3 (s), 125.8 (d), 128.2 (d), 133.9 (s), 137.2 (s); MS m/z 354 (M^+). **21**: pale yellow crystals, mp 227.0–228.5 °C; ^{1}H NMR δ 0.75 (s, 6 H), 1.40 (s, 6 H), 2.36 (s, 6 H), 7.16 (d, J = 8 Hz, 4 H), 7.47 (d, J = 8 Hz, 4 H); ^{13}C NMR δ 24.8 (q), 26.9 (q), 58.3 (s), 93.3 (s), 128.3 (d), 128.8 (d), 133.5 (s), 138.5 (s); MS m/z (relative intensity) 386 (M^+, 3), 322 (100), 307 (51), 145 (47). Anal. Calcd for $C_{22}H_{26}S_3$: C, 68.34; H, 6.78. Found: C, 67.90; H, 6.77.

Thermal Isomerization of a Mixture of 1,3-Dithietanes 4a and 14. A mixture of **4a** (0.1 mmol) and **14** (0.1 mmol) contaminated with **21** in benzene (5 mL) was heated for 6 h at reflux. HPLC analysis (flow rate: 1 mL/min) of the mixture showed two peaks due to disulfides **2** (t_R 3.3 min) and **15** (t_R 4.2 min) in addition to unreacted **21** (t_R 5.5 min).

Sulfurization of Benzophenone with 6. A mixture of **6** (271 mg, 0.5 mmol) and benzophenone (91 mg, 0.5 mmol) in toluene (10 mL) was refluxed under N_2 for 4 h and the resulting blue solution was cooled to room temperature. An aliquot (1 mL) of this solution was taken out and diluted to 50 mL with hexane. The yield of thiobenzophenone was estimated to be 92% by determining the intensity of the absorption due to thiobenzophenone (λ_{max} 609 nm, ϵ = 184[19]) in the visible spectrum. 1,3-Dithietane **4b** (140 mg, 95%) was obtained by chromatographic workup of the whole reaction mixture.

Sulfurization of Benzophenone with 17. A mixture of **17** (106 mg, 0.263 mmol) and benzophenone (50 mg, 0.27 mmol) in toluene (5 mL) was heated under reflux for 1 h. A portion (1 mL) of the mixture was taken out and was submitted to visible spectrum analysis, which revealed that the yield of thiobenzophenone is 68%.

Registry No. 1a, 34733-56-7; **1b**, 95581-35-4; **1c**, 125611-53-2; **1d**, 125611-54-3; **2**, 125611-55-4; **3a**, 125611-56-5; **3c**, 125611-57-6; **4a**, 125611-58-7; **4b**, 125611-59-8; **4c**, 125611-60-1; **6**, 125611-61-2; **7c**, 125611-62-3; **7d**, 125611-63-4; **8c**, 125611-64-5; **8d**, 125611-65-6; **9**, 125611-66-7; **10**, 97584-63-9; **14**, 125611-67-8; **15**, 125611-68-9; **17**, 82998-27-4; **20**, 125611-69-0; **21**, 125611-70-3; bromobenzene, 108-86-1; 2,5-dicyano-2,5-dimethylhexane, 10526-16-6; 2,6-dicyano-2,6-dimethylheptane, 2941-36-8; isobutyrophenone, 611-70-1; benzophenone, 119-61-9; thiobenzophenone, 1450-31-3.

Manganese(III)-Based Oxidative Free-Radical Cyclization of Unsaturated β-Keto Esters, 1,3-Diketones, and Malonate Diesters

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Oxidative free-radical cyclizations of unsaturated β-keto esters, 1,3-diketones, and malonate diesters with 2 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ are described. Oxidation of β-keto ester **1** with Mn(III) to enol radical **2** followed by 6-exo cyclization gives radical **4**, which is oxidized by Cu(II) to give alkene **7** in 64–71% yield. Oxidation of **9** gives a lower yield of 5-exo cyclization product **11** due to competing overoxidation to give **13**. Oxidative cyclization of **18** gives the tertiary radical **19**, which is further oxidized to cation **20**. Oxidation of α-substituted β-keto esters **23**, **33**, and **37** proceeds in high yield since the product cannot be oxidized further. Oxidative cyclization of unsaturated cyclic β-keto esters **40a** and **45** proceeds efficiently to give bicyclic adducts **42**, **44**, and **47**. Oxidative cyclizations of 4-alkenyl-2-methylcyclopentane-1,3-diones **54**, **61**, and **64** provide bicyclo[3.2.1]octanediones **57**, **63**, and bicyclo[3.3.1]nonanediones **66** and **67** in moderate yields. These studies indicate that Mn(III)-based oxidative free-radical cyclization is a powerful synthetic method, delineate the scope and limitations of this reaction, and suggest further avenues for exploration.

In the past decade free-radical cyclization of alkenes has become a valuable method for the synthesis of cyclic compounds.[1] The most widely used method is the reduction of a halide or other functional group to a radical

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