

Preparation and Thermal Isomerization of β -Arylthio α,β -Unsaturated Thioketone Dimer

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Synopsis. β -Arylthio α,β -unsaturated thioketone dimer, 3,6-diphenyl-4-arylthio-3-[2-(arylthio)ethenyl]-3,4-dihydro-1,2-dithiin, has been prepared. Thermal isomerization of 3,4-dihydro-1,2-dithiin (aryl=phenyl) afforded 6-phenyl-2,4-bis(phenylthio)-3-thiobenzoyl-3,4-dihydro-2H-thiopyran.

Several types of acyclic α,β -unsaturated thioketones have been reported. For example, aliphatic (1)¹⁾ or aromatic (4)^{2,3)} α,β -unsaturated thioketone is unstable at room temperature and exists in the dimeric form (2, 3, or 5). In contrast, β -thioxo enamines (6)⁴⁾ and α -(thioacyl)ketene dithioacetals (7)⁵⁾ are relatively stable and exist in monomeric forms. These results suggest that the thermal stability of acyclic α,β -unsaturated thioketone is influenced by the substituent groups, particularly heteroatoms (N or S), on the β -position.⁴⁾

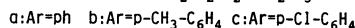
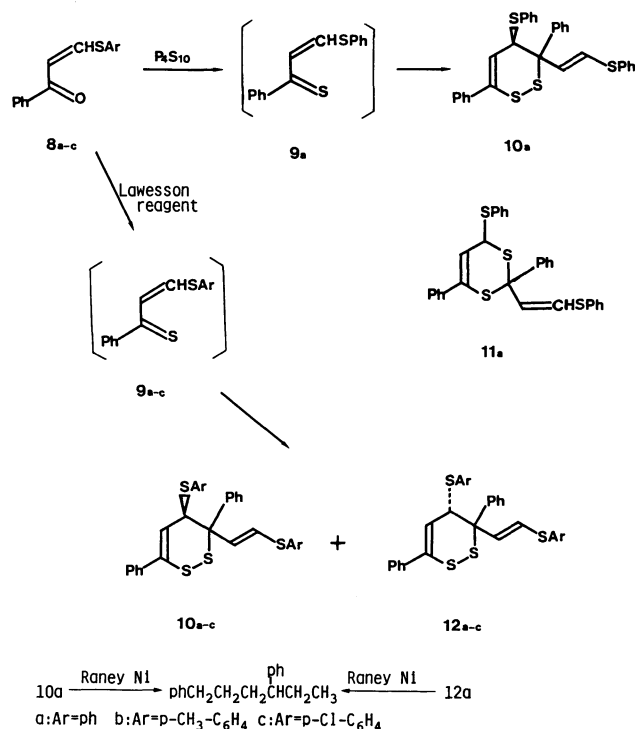
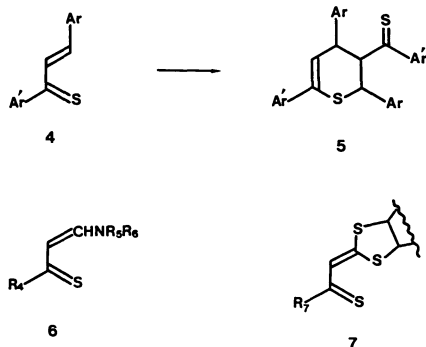
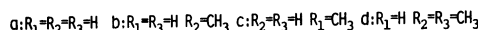
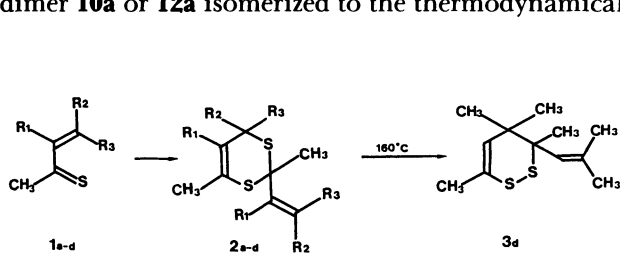
As a continuation of our investigation of α,β -unsaturated thioketones,^{3,6)} we have examined the preparation of β -arylthio α,β -unsaturated thioketone (9) in order to investigate the influence of the β -arylthio group on the stability of the α,β -unsaturated thioketone (9), and it was found that the thioketone 9 readily dimerized into 3,4-dihydro-1,2-dithiin compounds (10 and 12) at room temperature and the dimer 10a or 12a isomerized to the thermodynamical-

ly more stable dimer, the 3,4-dihydro-2H-thiopyran derivative (13a), at elevated temperature.

The reaction of 1-phenyl-3-phenylthio-2-propene-1-one (8a) with P₄S₁₀ gave two products together with a large amount of tarry matter.

In the ¹H-NMR spectrum of one product, doublets at δ 6.13 ($J=14.8$ Hz) and 6.70 ($J=14.8$ Hz) were assigned to olefinic protons in an *E*-configuration. An assignment of the C-4 proton to the axial position is supported by the coupling constant ($J=3.2$ Hz) between the C-4 and the C-5 protons.^{7,8)} The ¹³C-NMR spectrum exhibited two alkyl carbon signals at δ 55.2 (s) and 58.4 (d). These spectral data are in agreement with the proposed structure 10a or 11a. A treatment of this product with Raney nickel (W-2) gave 1,4-diphenylhexane. Therefore, this product was determined to be the 3,4-dihydro-1,2-dithiin structure 10a.

The ¹H-NMR spectrum of the other product showed three olefinic protons at δ 6.33 and one methine proton at δ 4.42. In the ¹³C-NMR spectrum appeared two alkyl carbon signals. However, it could not be determined whether the product was the 3,4-dihydro-1,2-dithiin or the 4H-1,3-dithiin structure.

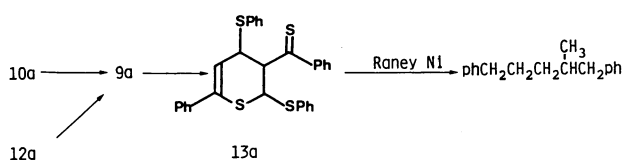


On the other hand, when **8a** was treated with Lawesson reagent while refluxing carbon disulfide, **10a** and **12a** were obtained. The structural assignment of **12a** is based on the ^1H -NMR spectrum and its conversion into 1,4-diphenylhexane by a Raney nickel reduction. The assignment of a C-4 proton to the equatorial position is supported by the larger coupling constant ($J=5.2$ Hz) between the C-4 and the C-5 protons than that of **10a** and in comparison with that of the analogous 3,4-dihydro-1,2-dithiin in the literature.⁸⁾

3,4-Dihydro-1,2-dithiin was unstable during the course of isolation by column chromatography and recrystallization. Thus, the isolated yields were low. The thionation of other ketones **8b** and **8c** with Lawesson reagent afforded **12b** and **10c**, respectively. However, it was not possible to isolate **10b** and **12c** due to the ease of decomposition.

We observed that the color of solution (hexane, chloroform, etc) **10** or **12** turned from pale yellow to green upon heating. Thus, 3,4-dihydro-1,2-dithiin **10a** or **12a** was refluxed in hexane to give 3,4-dihydro-2*H*-thiopyran **13a** in moderate yield, respectively. The molecular ion (m/z 512) was observed in the mass spectrum. The ^{13}C -NMR spectrum exhibited a characteristic thiocarbonyl carbon signal at δ 235.5 and three methine carbon signals. Desulfurization of the dihydrothiopyran gave 2-methyl-1,5-diphenylpentane. Therefore, this compound was assigned to the proposed structure **13a**.

It would be probable that 3,4-dihydro-1,2-dithiin **10** and **12** formed by the cyclodimerization of **9** and the thermal unstable 3,4-dihydro-1,2-dithiin isomerized to the thermodynamically more stable dihydrothiopyran via a retro-Diels-Alder reaction at an elevated temperature (Scheme 1). The β -arylthio group, especially when there was only one sulfur atom, did not contribute to the stabilization of monomer **9**.



Scheme 1.

Experimental

All melting points were uncorrected. ^1H -NMR spectra were determined on a JEOL JNM PMX60SI or FX-100 spectrometer and ^{13}C -NMR spectra were recorded on a JEOL JNM-FX-100 spectrometer. Me_4Si was used as an internal standard. Mass spectra were measured on a Hitachi mass spectrometer RMU-7M or a JEOL JMS-DX300 or JMA-3100 mass spectrometer. 2,4-Bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide (Lawesson reagent) was obtained commercially. All 1-phenyl-3-arylthio-2-propene-1-ones (**8**) were prepared according to the method of Engelhard et al.⁹⁾

Thionation with P_4S_{10} . A suspension of 1-phenyl-3-phenylthio-2-propene-1-one **8a** (2.4 g), P_4S_{10} (1.0 g), and

triethylamine (1.0 ml) in carbon disulfide (80 ml) was stirred at room temperature for 6 d. The solvent was evaporated and the residue was chromatographed on a Florisil gel by using benzene-hexane (1:1) as the eluent.

The first fraction was determined to be 3,6-diphenyl-4-phenylthio-3-[2-(phenylthio)ethenyl]-3,4-dihydro-1,2-dithiin **10a**: yellow rhombic crystals. Mp 102–104 °C. yield 3.9%. MS (22 eV) m/z : 256 ($\text{M}^+ - 2$, 5.8), 179 (100), 147 (3.9), 121 (11.7), 110 (18). ^1H -NMR (CDCl_3) δ =4.58 (1H, d, $J=3.2$ Hz), 6.13 (1H, d, $J=14.8$ Hz), 6.50 (1H, d, $J=3.2$ Hz), 6.70 (1H, d, $J=14.8$ Hz), 7.10–7.67 (20H, m). ^{13}C -NMR (CDCl_3) δ =55.2 (s), 58.4 (d), 126.3, 127.1, 127.5, 127.8, 128.4, 128.8, 129.1, 132.4, 135.0, 136.6, 137.8, 141.3. Found: C, 70.00; H, 4.72%. Calcd for $\text{C}_{30}\text{H}_{24}\text{S}_4$: C, 70.27; H, 4.66%.

The second fraction: yellow silky needles. Mp 116–117.5 °C. yield 1.8%. MS (22 eV) m/z : 256 ($\text{M}^+ - 2$, 8), 179 (100), 147 (64), 121 (18), 115 (10), 110 (10), 103 (11). ^1H -NMR (CDCl_3) δ =4.42 (1H, d, $J=4.8$ Hz), [6.33 (d, $J=4.8$ Hz), 6.33 (s) total 3H], 7.23–7.70 (20H, m). ^{13}C -NMR (CDCl_3) δ =55.5 (d), 63.9 (s), 123.3, 125.9, 126.6, 127.0, 127.3, 127.9, 128.5, 128.9, 129.1, 129.8, 132.1, 132.6, 135.7, 135.9, 138.0, 138.3. Found: C, 70.03; H, 4.66%. Calcd for $\text{C}_{30}\text{H}_{24}\text{S}_4$: C, 70.27; H, 4.66%.

Thionation with Lawesson Reagent. A suspension of **8a** (2.4 g) and Lawesson reagent (2.0 g) in carbon disulfide (20 ml) was refluxed for 5 h under a nitrogen atmosphere. The solvent was removed using a rotary evaporator and the residue was passed through a short column of Florisil gel using benzene-hexane (1:1) as the eluent to give a mixture of **10a** and **12a** (yield 46%). The mixture was chromatographed on Florisil gel using benzene-hexane (1:3) as the eluent.

10a: Yield 13% (recrystallized from benzene-hexane).

12a: Yellow silky needles (recrystallized from benzene-ethanol). Mp 99.5–101.5 °C. yield 7.8%. ^1H -NMR (CDCl_3) δ =4.27 (1H, d, $J=5.2$ Hz), 6.23 (1H, d, $J=15.2$ Hz), 6.40 (1H, d, $J=15.2$ Hz), 6.52 (1H, d, $J=5.2$ Hz), 6.97–7.45 (20H, m). ^{13}C -NMR (CDCl_3) δ =57.1 (d), 58.4 (s), 126.1, 126.3, 126.8, 127.0, 127.3, 127.7, 127.8, 128.3, 128.6, 128.7, 128.9, 129.1, 129.8, 132.2, 134.0, 134.6, 136.0, 136.5, 138.0, 139.4. Found: C, 70.11; H, 4.57%. Calcd for $\text{C}_{30}\text{H}_{24}\text{S}_4$: C, 70.27; H, 4.66%.

4-(*p*-Methylphenylthio)-3,6-diphenyl-3-[2-(*p*-methylphenylthio)ethenyl]-3,4-dihydro-1,2-dithiin **12b:** Mp 108–109 °C. yield 8%. MS (20 eV) m/z : 416 (2), 385 (6), 293 (30), 179 (100). ^1H -NMR (CDCl_3) δ =2.27 (6H, s), 4.22 (1H, d, $J=5.2$ Hz), 6.14 (1H, d, $J=15.2$ Hz), 6.50 (1H, d, $J=15.2$ Hz), 6.55 (1H, d, $J=5.2$ Hz), 6.85–7.47 (18H, m). Found: C, 71.01; H, 5.22%. Calcd for $\text{C}_{32}\text{H}_{28}\text{S}_4$: C, 71.07; H, 5.22%.

***p*-(Chlorophenylthio)-3,6-diphenyl-3-[2-(*p*-chlorophenylthio)ethenyl]-3,4-dihydro-1,2-dithiin **10c**:** Mp 122–126 °C. yield 22%. MS (20 eV) m/z : 436, 408, 406, 404, 320, 318, 298, 296, 180, 144. ^1H -NMR (CDCl_3) δ =4.52 (1H, d, $J=3.2$ Hz), 6.10 (1H, d, $J=16.0$ Hz), 6.43 (1H, d, $J=3.2$ Hz), 6.57 (1H, d, $J=16.0$ Hz), 6.93–7.60 (18H, m). Found: C, 61.59; H, 3.82%. Calcd for $\text{C}_{30}\text{H}_{22}\text{Cl}_2\text{S}_4$: C, 61.95; H, 3.81%.

Reduction of **10a with Raney Nickel.** To a suspension of freshly prepared W-2 Raney nickel¹⁰⁾ (≈ 10 g) in ethanol (20 ml) was added 1,2-dithiin **10a** (1.0 g) in benzene (20 ml). The mixture was stirred overnight at room temperature. The mixture was chromatographed on Wakogel C-200 using hexane as the eluent to give 1,4-diphenylhexane: yield 0.3 g (65%). MS (20 eV) m/z : 238 ($\text{M}^+ - 2$), 131 (69), 119 (23), 105 (19), 91 (100). ^1H -NMR (CDCl_3) δ =0.62–2.63 (12H, m), 7.08 (10H). ^{13}C -NMR (CDCl_3) δ =12.3, 29.5, 29.9, 36.1, 47.9, 125.7, 125.9, 127.9, 128.3, 128.5, 142.7, 145.8.

Reduction of **12a with Raney Nickel.** 1,4-Diphenylhexane: yield 94%.

Reduction of 13a with Raney Nickel. To a suspension of freshly prepared W-2 Raney nickel¹⁰ (≈ 10 g) in benzene (100 ml) was added dihydrothiopyran **12a** (0.5 g). The mixture was stirred overnight at room temperature. Purification of the mixture by preparative TLC (Merk 5744) using benzene-hexane (1:3) as the eluent gave 2-methyl-1,5-diphenylpentane: yield 73 mg (31%). MS (70 eV) m/z : 238 (M^+ , 17), 147 (12), 131 (12), 91 (100). $^1\text{H-NMR}$ (CDCl_3) δ =0.83 (3H, d), 1.17–1.93 (5H, m), 2.13–2.80 (4H, m), 7.10 (10H, s). $^{13}\text{C-NMR}$ (CDCl_3) δ =19.3 (t), 29.1 (t), 34.9 (d), 36.1 (t), 36.3 (t), 43.6 (t).

Thermal Isomerization of 10a. A suspension of **10a** (1.145 g) in hexane (100 ml) was refluxed for 9 h under a nitrogen atmosphere. The resulting deep-blue precipitate was collected by filtration and washed with ethanol. The precipitate was recrystallized from benzene-hexane to give 6-phenyl-2,5-bis(phenylthio)-3-thiobenzoyl-3,4-dihydro-2H-thiopyran **13a** as a deep blue needles: Mp 128–129 °C. yield 0.894 g (78%). MS (FD) m/z : 512 (M^+). $^1\text{H-NMR}$ (CDCl_3) δ =[4.46 (J =3.6, 7.0, and 0.2 Hz), 4.50 (J =3.6, 4.0, and 0.2 Hz) total 2H], 5.09 (1H, J =7.0, 0.2, and 0.1 Hz), 6.20 (1H, J =4.0, 0.2, and 0.1 Hz), 7.08–7.56 (20H, m). $^{13}\text{C-NMR}$ (CDCl_3) δ =47.2 (d), 51.2 (d), 55.6 (d), 119.5, 126.4, 126.5, 127.4, 128.9, 129.1, 129.4, 131.9, 132.1, 132.9, 133.7, 134.4, 135.6, 138.2, 145.8, 235.5. Found: C, 70.30; H, 4.56%. Calcd for $\text{C}_{30}\text{H}_{24}\text{S}_4$: C, 70.27; H, 4.66%.

Thermal Isomerization of 12a. **13a**: yield 53%.

References

- 1) W. J. Bailey and M. Izogawa, *Am. Chem. Soc. Div.*

Polymer Chem. Preprints **14**, 300 (1973); H. G. Giles, R. A. Marty, and P. deMayo, *J. Chem. Soc., Chem. Commun.*, **1974**, 409; H. G. Giles, R. A. Marty, and P. deMayo, *Can. J. Chem.*, **54**, 537 (1976); P. Beslin, D. Lagain, and J. Vialle, *Tetrahedron Lett.*, **1979**, 2677; P. Beslin, D. Lagain, J. Vialle, and C. Monot, *Tetrahedron*, **37**, 3839 (1981); P. Beslin, *J. Heterocyclic Chem.*, **20**, 1753 (1983).

2) J. P. Pradere, G. Bouet, and H. Quiniou, *Tetrahedron Lett.*, **1972**, 3471.

3) T. Karakasa and S. Motoki, *J. Org. Chem.*, **43**, 4147 (1978).

4) H. Quiniou, *Phosphorus and Sulfur*, **10**, 1 (1981); V. A. Usov and M. G. Voronkov, *Sulfur Reports*, **2**, 39 (1982) and references therein.

5) R. Okazaki, K. Okawa, and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, **1971**, 843; R. Okazaki, F. Ishii, K. Ozawa, and N. Inamoto, *Chem. Lett.*, **1972**, 9; F. Ishii, K. Okawa, and N. Inamoto, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 270.

6) T. Karakasa and S. Motoki, *J. Org. Chem.*, **44**, 4151 (1979); T. Karakasa, H. Yamaguchi, and S. Motoki, *ibid.*, **45**, 927 (1980); T. Karakasa and S. Motoki, *Chem. Lett.*, **1980**, 879.

7) P. M. Henrichs and C. H. Chen, *J. Org. Chem.*, **44**, 3591 (1979).

8) J-P. Guemas and H. Quiniou, *Sulfur Letters*, **2**, 121 (1984).

9) N. Engelhard and A. Kolb, *Justus Liebigs Ann. Chem.*, **673**, 136 (1964).

10) R. Mozingo, *Org. Synth.*, Coll. Vol. **3**, 181 (1954).