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-2*H*-thiopyran.

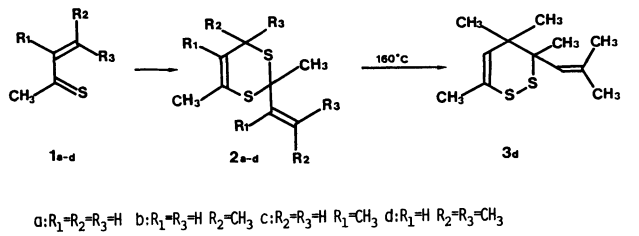
Several types of acyclic α,β-unsaturated thioketones have been reported. For example, aliphatic (**1**)[1] or aromatic (**4**)[2,3] α,β-unsaturated thioketone is unstable at room temperature and exists in the dimeric form (**2**, **3**, or **5**). In contrast, β-thioxo enamines (**6**)[4] and α-(thioacyl)ketene 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]

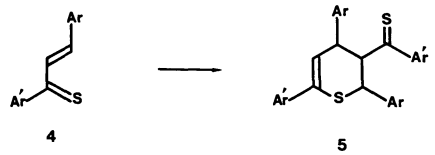
As a continuation of our investigation of α,β-unsaturated thioketones,[3,6] we have examined the preparation of β-arylthio α,β-unsaturated thioketone (**9**) in order to investigate the influence of the β-arylthio group on the stability of the α,β-unsaturated thioketone (**9**), and it was found that 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 thermodynamically more stable dimer, the 3,4-dihydro-2*H*-thiopyran derivative (**13a**), at elevated temperature.

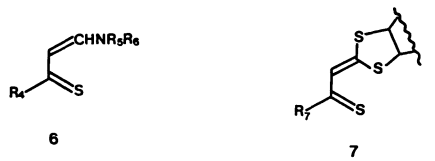
The reaction of 1-phenyl-3-phenylthio-2-propene-1-one (**8a**) with P_4S_{10} gave two products together with a large amount of tarry matter.

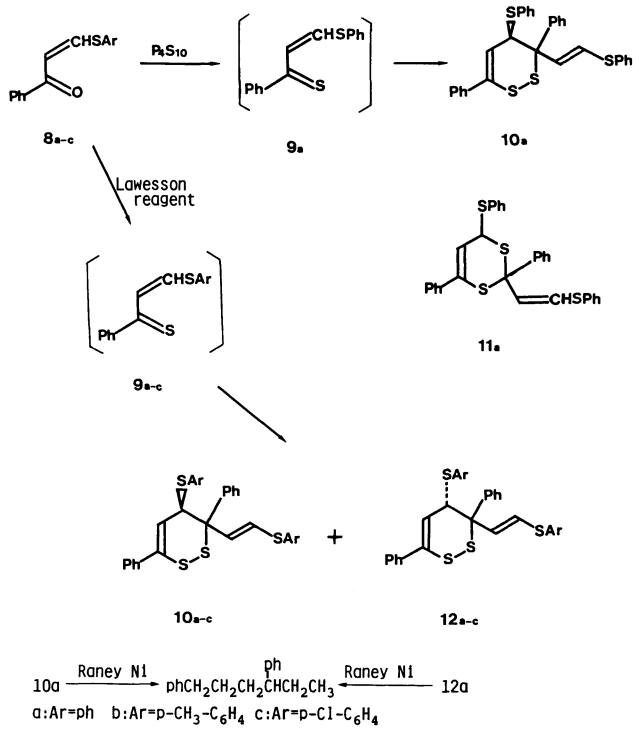
In the ^{1}H-NMR spectrum of one product, doublets at δ 6.13 (J=14.8 Hz) and 6.70 (J=14.8 Hz) were assigned to olefinic protons in an *E*-configuration. An assignment of the C-4 proton to the axial position is supported by the coupling constant (J=3.2 Hz) between the C-4 and the C-5 protons.[7,8] The ^{13}C-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 ^{1}H-NMR spectrum of the other product showed three olefinic protons at δ 6.33 and one methine proton at δ 4.42. In the ^{13}C-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 4*H*-1,3-dithiin structure.







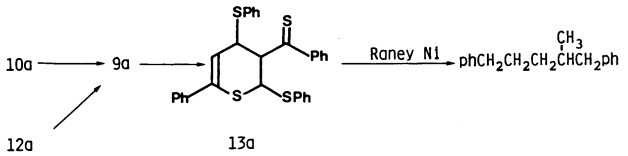


On the other hand, when **8a** was treated with Lawesson reagent while refluxing carbon disulfide, **10a** and **12a** were obtained. The structural assignment of **12a** is based on the ^{1}H-NMR spectrum and its conversion into 1,4-diphenylhexane by a Raney nickel reduction. The assignment of a C-4 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 contributed to the stabilization of monomer **9**.



Scheme 1.

Experimental

All melting points were uncorrected. ^{1}H-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-7 M 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 ($M^+/2$, 5.8), 179 (100), 147 (3.9), 121 (11.7), 110 (18). ^{1}H-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 $C_{30}H_{24}S_4$: 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 ($M^+/2$,8), 179 (100), 147 (64), 121 (18), 115 (10), 110 (10), 103 (11). ^{1}H-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 $C_{30}H_{24}S_4$: 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%. ^{1}H-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 $C_{30}H_{24}S_4$: 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). ^{1}H-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 $C_{32}H_{28}S_4$: 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. ^{1}H-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 $C_{30}H_{22}Cl_2S_4$: C, 61.95; H, 3.81%.

Reduction of 10a with Raney Nickel. To a suspension of freshly prepared W-2 Raney nickel[10] (≃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 (M^+, 23), 131 (69), 119 (23), 105 (19), 91 (100). ^{1}H-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 nickel[10] (≃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}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}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 benzen–hexane to give 6-phenyl-2,5-bis(phenylthio)-3-thiobenzoyl-3,4-dihydro-2*H*-thiopyran **13a** as a deep blue needles: Mp 128—129 °C. yield 0.894 g (78%). MS (FD) *m/z*: 512 (M^+). ^{1}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}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 $C_{30}H_{24}S_4$: C, 70.27; H, 4.66%.

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

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