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Synthesis of New Type Stable Heterotriene. Conjugated Dienic Thioketone

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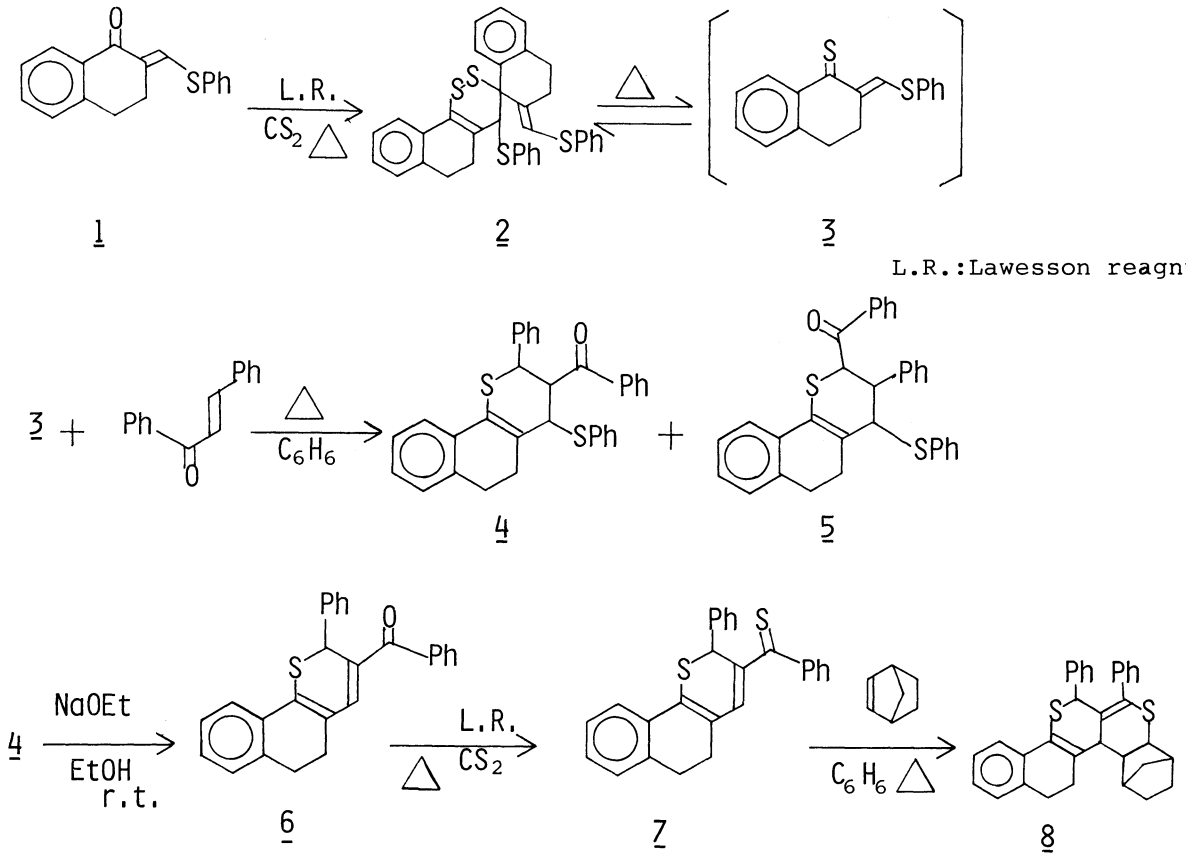
2-Phenyl-3-thiobenzoyl-5,6-dihydrobenzo[*h*]-2*H*-thiochromene was synthesized in 4 steps from 2-(phenylthio)methylene-1-tetralone. The thione reacted as a heterodiene with norbornene to give the corresponding [4+2]cycloadduct.

The chemistry of heterotrienes such as dienones and azatrienes has been widely investigated.[1] In contrast to studies of these heterotrienes, little attention has been paid to conjugated dienic thioketones.[2] Considering the wealth of chemistry exhibited by these heterotrienes, synthesis and reaction of conjugated dienic thioketones are attractive subjects. For example, Brandsma et al.[3] reported that conjugated dienic thioketones were derived as unstable intermediates from allenic thioketones formed by the thio-Claisen rearrangement of 2-alkynyl vinyl sulfides. However, so far as we know, there is apparently no case in which a conjugated dienic thioketone was isolated. Also, an attempt to prepare the 1,5-diphenyl-2,4-pentadiene-1-thione monomer by the thionation of the corresponding dienone was unsuccessful.[4]

During the course of an investigation of the cycloaddition of β-arylthio α,β-unsaturated thioketones[5] with electronwithdrawing dienophiles, we found that the elimination of thiophenol from the obtained cycloadduct took place by the action of sodium ethoxide. Interest in this elimination has led to the synthesis of dienic thioketone **7** employing the β-arylthio-α,β-unsaturated thioketones **3** as the starting materials by sequence **3** → **4** → **6** → **7**.

A solution of 2-(phenylthio)methylenetetralin-1-thione dimer **2**[6] (1.00 g)

and chalcone (0.81 g) in dry benzene (10 cm^3) was refluxed for 2 h under nitrogen atmosphere. The solution gradually turned from green to pale yellow. After the reaction was over, the solvent was removed and the residue was chromatographed on Wakogel C-200 to give the desired dihydrothiopyran (**4**, colorless needles (recrystallized from ethanol), yield 59%, mp 178-181 °C) and its regioisomer (**5**, colorless needles (recrystallized from ethanol), yield 12%, mp 159-160 °C). The IR, MS (70 eV) and ^{1}H-NMR (60 MHz) spectral data supported the structures of **4** and **5**.[8] The dienic ketone **6** was easily derived from the cycloadduct **4** by elimination of thiophenol. To the solution of **4** (1.00 g) in dry benzene (20 cm^3) was added sodium ethoxide (sodium metal 0.25 g in ethanol 30 cm^3). After stirring overnight, the reaction mixture turned orange. Water was added to the mixture and the product was extracted with diethyl ether. The solvent was removed and the residue was chromatographed on Wakogel C-200 with ethyl acetate-hexane (1:4) to give yellow cubic crystals (**6**, recrystallized from diethyl ether-hexane, yield 90%, mp 129-130 °C).[9]



Scheme 1.

Thionation of the dienone **6** was performed with Lawesson reagent. The suspension of **6** (0.95 g) and Lawesson reagent (0.70 g) in carbon disulfide (30 cm^3) was refluxed for 5 h under nitrogen atmosphere. The solution turned dark red. Then the solvent was removed and the residue was passed through a short column of Florisil gel using benzene-hexane (1:1) to give the dienic thioketone **7** (red crystals (recrystallized from hexane), yield 55%, mp 72-74 °C). Existence of **7** in monomeric form was conformed by the IR, MS and NMR spectra.[10] Usually, α,β-unsaturated thioketones dimerize readily by self-cycloaddition reaction.[5,11] However, thioketones such as 2-cyclohexenethione or 2-cyclopentenethione,[12] where C=C and C=S double bonds are constrained in a transoid form, do not take part in dimerization and exist in monomeric form. Judging from the molecular model, **7** is considered to have the transoid conformation regarding C=C-C=S moiety, because the cisoid conformation represented in Fig. 1 would be less stable than the transoid on account of the mutual repulsion between the two phenyl groups.

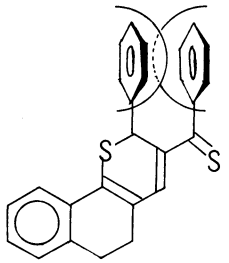


Fig. 1.

Finally, we have been interested in the cycloaddition reaction of the thioketone **7**. The solution of **7** (0.11 g) and norbornene (0.30 g) in dry benzene (10 cm^3) was refluxed for 4 h under nitrogen atmosphere. The solution turned from red to colorless. The solvent was removed and the residue was chromatographed on Wakogel C-200 to give the corresponding [4+2]cycloadduct (**8**, colorless crystals (recrystallized from hexane), yield 50%, mp 226-227 °C).[13] In a similar way, cycloadducts with some other dienophiles were obtained, the results of which will be reported at a later date.

References

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6) 2-(Phenylthio)methylene-1-tetralone **1** was prepared by the method modified from that of Engelhard et al.[7] and the thione dimer **2** was prepared according to the method described in the previous report.[5] **1**: yellow needles; mp 59-61 °C; IR (KBr) 1651 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 2.92 (s, 4H), 7.03-7.63 (m, 7H), 7.77-8.20 (m, 2H). 2-(Phenylthio)methylenetetralin-1-thione dimer **2**: yield 46%; colorless needles; mp 120-122 °C; ^{1}H-NMR ($CDCl_3$) δ 2.10-3.05 (m, 8H), 4.77 (s, 1H), 6.40 (s, 1H), 6.63-7.97 (m, 13H); MS m/z 282 ($M^+/2$, 7), 205 ($M^+/2$-Ph, 100), 171 ($M^+/2$-Ph-H_2S, 7).

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8) 3-Benzoyl-2-phenyl-4-phenylthio-5,6-dihydrobenzo[*h*]thiochromane **4**: IR (KBr) 1688 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 2.22-2.98 (m, 4H), 4.13 (d, 1H, J=2.8 Hz), 4.60 (dd, 1H, J=2.8, 10.8), 5.17 (d, 1H, J=10.8), 6.88-7.47 (m, 19H); MS m/z 380 (M^+-PhSH, 5), 275 (M^+-PhSH-PhCOH, 22), 205 (Thione$^+$-Ph, 100). The isomer **5**: IR (KBr) 1700 cm^{-1} (C=O); ^{1}H-NMR δ 2.30-2.83 (m, 4H), 3.87 (d, 1H, J=2.8 Hz), 4.05, (dd, 1H, J=2.8, 10.8), 5.67 (d, 1H, J=10.8), 6.87-7.44 (m, 17H), 7.83-7.93 (m, 2H).

9) 3-Benzoyl-2-phenyl-5,6-dihydrobenzo[*h*]-2*H*-thiochromene **6**: IR (KBr) 1632 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 2.23-2.80 (m, 4H), 5.57 (s, 1H), 6.98-7.68 (m, 15H); ^{13}C-NMR δ 28.6 (t), 28.1 (t), 39.3 (d), 195.6 (s, C=O); MS m/z 380 (M^+, 3), 275 (M^+-PhCO, 100), 241 (M^+-Ph-H_2S, 56).

10) 2-Phenyl-3-thiobenzoyl-5,6-dihydrobenzo[*h*]-2*H*-thiochromene **7**: IR (KBr) 1148 cm^{-1} (C=S); ^{1}H-NMR ($CDCl_3$) δ 2.22-2.92 (m, 4H), 6.27 (s, 1H), 7.00-7.62 (m, 15H); ^{13}C-NMR δ 28.2 (t), 28.6 (t), 42.9 (d), 126.0 , 126.3, 126.9, 127.4, 127.7, 127.9, 128.2, 129.1, 129.5, 132.7, 135.3, 137.0, 137.3, 138.3, 140.7, 148.8, 230.7 (s, C=S); MS m/z 396 (M^+, 100), 363 (M^+-SH, 69), 287 (M^+-PhS, 28), 275 (M^+-PhCS, 69), 241 (23), 198 (9), 121 (39), 115 (14).

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13) The cycloadduct **8**: ^{1}H-NMR (60MHz, $CDCl_3$) δ 1.13-1.17 (m, 6H), 2.13-3.68 (m, 7H), 3.08-3.30 (m, 2H), 4.82 (s, 1H), 6.86-7.39 (m, 14H); MS m/z 490 (M^+, 45), 457 (63), 397 (100), 363 (57), 287 (20), 275 (35), 241 (12).

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