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Reactions of α,β-Unsaturated Thiones with Diphenylcyclopropenone and Diphenylcyclopropenethione

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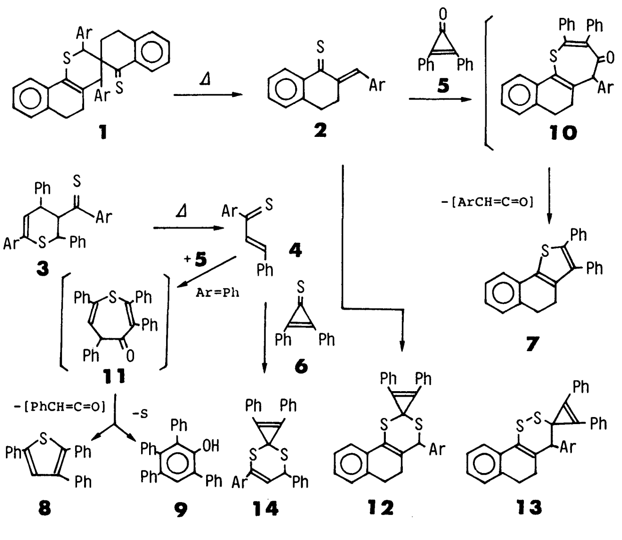
Synopsis. 2-(Arylmethylene)tetralin-1-thione and 1-aryl-3-phenyl-2-propene-1-thione (thiochalcone) reacted with diphenylcyclopropenone across the =C–CO bond giving a thiophene derivative and a polysubstituted phenol with the arylketene/sulfur elimination, whereas the reaction with diphenylcyclopropenethione took place at the C=S bond affording a spiro compound.

Cyclopropenones and cyclopropenethiones have been known to be highly reactive compounds. Especially, many informations on the chemistry of cyclopropenones have accumulated in numerous papers and their cycloadditions were found to occur across the C=O, C=C, or the C–CO bond of the ring.[1,2] Previously, we reported that the α,β-unsaturated thiones such as 2-(arylmethylene)tetralin-1-thiones (**2**) and thiochalcones (**4**), which were generated by thermolysis of their dimers **1** and **3**, underwent cycloaddition reactions with various dienophiles to give 1:1-adducts.[3] As a continuation of the work, reactions of these thiones with diphenylcyclopropenone (**5**) and diphenylcyclopropenethione (**6**) have been investigated in the present study.

A mixture of 2-(phenylmethylene)tetralin-1-thione dimer, **1a**, and **5** in dry benzene was refluxed for 2.5 h. After the reaction was completed, the mixture was chromatographed to give 4,5-dihydro-2,3-diphenylnaphtho[1,2-*b*]thiophene (**7**) in a yield of 57%. Evidently, the product showed no band for a carbonyl group in the IR spectrum, and the ^{1}H NMR spectrum exhibited only signals of ethylene protons (4H) and aromatic protons (14H). In the mass spectrum, a molecular ion peak was observed at m/z 338 (100% intensity) which corresponded to that of m/z 456 (1:1-adduct) -118 (C_8H_6O). Since it is obvious from these spectral data that not less than one phenyl moiety was eliminated from a 1:1-adduct, reactions of 2-(p-methoxybenzylidene)tetralin-1-thione dimer (**1b**) and 2-(p-chlorobenzylidene)tetralin-1-thione dimer (**1c**) with **5** were examined. The product obtained in each case was the same compound **7** in which no p-methoxy- or p-chlorophenyl moiety was contained. The reaction of thiochalcone dimer, **3a**, with **5** afforded 2,3,5-triphenylthiophene (**8**) and 2,3,4,6-tetraphenylphenol (**9**) (Table 1). These interesting results are rationalized in terms of the [4+3]cycloaddition of the α,β-unsaturated thiones (**2**, **4**) and **5** with fission of the =C–CO bond of **5** and the subsequent elimination of the arylketene/sulfur atom from the intermediary 1:1-adducts (**10**, **11**). However, attempt to trap the ketene by methanol was unsuccessful. On the other hand, treatment of **1a** with **6** in refluxing benzene for 1 h gave a 1:1-adduct in a yield of 56%. The ^{1}H and ^{13}C NMR spectra of the adduct indicated the presence of a ethylene group, a methine group, and a quarternary carbon atom of the cyclopropene ring in addition to the olefinic and the aromatic moieties. The results suggest that both regioisomeric structures, **12** and **13**, are plausible for the adduct. We prefer the 1,3-dithiin structure because their mass fragmentation pattern[4] showed extrusion of a thiobenzaldehyde molecule from **12**, not from **13**. Similarly, the reactions of **1b**, **c** and **3a**—**c** with **6** gave the 1,3-dithiins **12b**, **c** and **14a**—**c**, respectively (Table 1).

Marked contrast between the reactions of the α,β-unsaturated thiones (**2**, **4**) with **5** and **6** can be recognized by the fact that thiocarbonyl group is usually more susceptible than carbonyl group to various addition reactions.[5] Actually, **2** and **4** react readily with ordinary thioketones such as thiobenzophenone to give the similar 1,3-dithiin adducts, whereas no reaction takes



	Ar
a	C_6H_5
b	p-$MeOC_6H_4$
c	p-ClC_6H_4

Table 1. Reaction of the Thione Dimers (**1**, **3**) with Diphenylcyclopropenone (**5**) and Diphenylcyclopropenethione (**6**)

Thione dimer	Dienophile	Reaction time/h	Product	Mp, θ_m/°C	Yield/%
1a	5	2.5	**7**		57
1b	5	1.5	**7**	166—168	52
1c	5	3.0	**7**		59
3a	5	8.0	**8**	132—134[a]	37
			9	96—97	19
1a	6	1.5	**12a**	200—202	56
1b	6	1.5	**12b**	204—206	63
1c	6	0.5	**12c**	203—205	59
3a	6	1.0	**14a**	146—147	62
3b	6	0.5	**14b**	176—178	88
3c	6	0.5	**14c**	160—163	62

a) Lit 9; mp 127 °C, lit 10; mp 157 °C.

place with ketones or aldehydes under the same reaction conditions.[6]

Experimental

All melting points are uncorrected. IR spectra were measured on a Hitachi Model 260-10 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer and/or a JEOL PMX-60SI spectrometer in a $CDCl_3$ solution using tetramethylsilane as an internal standard. Mass spectra were recorded on a Hitachi double focusing mass spectrometer RMU-7M and/or M-80 with a data processing system M-003, operating at an ionizing potential of 100 or 70 eV. Elemental analyses were performed using a Yanagimoto Model MT-3 CHN corder.

2-(Arylmethylene)tetraline-1-thione dimers (**1a**—**c**) and thiochalcone dimers (**3a**—**c**) were prepared according to the method described previously.[3] Diphenylcyclopropenone (**5**)[7] and diphenylcyclopropenethione (**6**)[8] were prepared by the method given in the literature.

General Procedure for Reaction of the Thione Dimers (1, 3) with Diphenylcyclopropenone (5) or Diphenylcyclopropenethione (6). A mixture of **1** or **3** (4 mmol as a monomer) and **5** or **6** (4 mmol) in dry benzene (6 ml) was refluxed for a required period under a nitrogen atmosphere. After the reaction was completed, the solvent was removed and the residue was chromatographed on silica gel (Wakogel C-200) with benzene–hexane as an eluent. The crude product was recrystallized from an appropriate solvent.

4,5-Dihydro-2,3-diphenylnaphtho[1,2-*b*]thiophene (7). ^{1}H NMR δ=2.52—2.96 (m, 4H, CH_2CH_2), 7.04—7.40 (m, 14H, Ar–H); MS *m/z* 338 (100, M^+), 304 (5, $M^+{-}H_2S$), 261 (8, $M^+{-}Ph$); Found: M^+ 338.1131; Found: C, 85.03; H, 5.37%. Calcd for $C_{24}H_{18}S$: C, 85.17; H, 5.36%; M, 338.1129.

2,3,5-Triphenylthiophene (8). Colorless fluffy needles; IR (KBr) 1605, 765, and 705 cm^{-1}; ^{1}H NMR δ=7.0—7.7 (m, =CH, Ar–H); MS *m/z* 312 (100, M^+), 278 (14, $PhCCPh^+$), 191 (6, $M^+{-}PhCS$), 121 (13, $PhCS^+$).

2,3,4,6-Tetraphenylphenol (9). Yellow crystals; IR (KBr) 3440 cm^{-1}; ^{1}H NMR δ=6.73 (s, 1H, OH), 6.9—7.8 (m, 21H, Ar–H); MS *m/z* 398 (100, M^+), 321 (39, $M^+{-}Ph$), 293 (55, $M^+{-}Ph{-}CO$), 215 (32, $M^+{-}2Ph{-}COH$), 105 (72, $PhCO^+$).

5′,6′-Dihydro-2,3,4′-triphenylspiro[2-cyclopropene-1,2′-[4*H*]-naphtho[1,2-*d*][1,3]dithiin] (12a). ^{1}H NMR δ=2.82 (m, 4H, CH_2CH_2), 5.51 (s, 1H, CH–Ph), 7.0—7.7 (m, 19H, Ar–H); ^{13}C NMR δ=26.3 (t, CH_2CH_2), 28.5 (t, CH_2CH_2), 56.0 (d, C(1)), 70.2 (s, spiro-C(3)); MS *m/z* 472 (77, M^+), 440 (11, $M^+{-}S$), 350 (100, $M^+{-}PhCS$); Found: M^+ 472.1315. Found: C, 81.61; H, 5.19%. Calcd for $C_{32}H_{24}S_2$: C, 81.32; H, 5.12%; M, 472.1318.

5′,6′-Dihydro-4′-(*p*-methoxyphenyl)-2,3-diphenylspiro[2-cyclopropene-1,2′-[4*H*]naphtho[1,2-*d*][1,3]dithiin] (12b). ^{1}H NMR δ=2.82 (m, 4H, CH_2CH_2), 3.64 (s, 3H, OCH_3), 5.48 (s, 1H, CH–Ar), 6.5—7.7 (m, 18H, Ar–H); ^{13}C NMR δ=26.2 (t, CH_2CH_2), 28.6 (t, CH_2CH_2), 55.1 (d, C(1)), 55.8 (q, OCH_3), 70.5 (s, spiro-C(3)); MS *m/z* 502 (65, M^+), 470 (16, $M^+{-}S$), 350 (100, $M^+{-}ArCHS$). Found: C, 78.74; H, 5.01%. Calcd for $C_{33}H_{26}S_2$; C, 78.85; H, 5.21%.

5′,6′-Dihydro-4′-(*p*-chlorophenyl)-2,3-diphenylspiro[2-cyclopropene-1,2′-[4*H*]naphtho[1,2-*d*][1,3]dithiin] (12c). ^{1}H NMR δ=2.78 (m, 4H, CH_2CH_2), 5.40 (s, 1H, CH–Ar), 7.0—7.7 (m, 18H, Ar–H); ^{13}C NMR δ=26.3 (t, CH_2CH_2), 28.5 (t, CH_2CH_2), 55.1 (d, C(1)), 75.7 (s, spiro-C(3); MS *m/z* 507 (21, M^+), 475 (10, $M^+{-}S$), 350 (100, $M^+{-}ArCHS$). Found: C, 75.46; H, 4.46%. Calcd for $C_{32}H_{23}S_2Cl$: C, 75.79; H, 4.57%.

2,3,4′,6′-Tetraphenylspiro[2-cyclopropene-1,2′-[4*H*][1,3]dithiin] (14a). ^{1}H NMR δ=5.38 (s, 1H, H(4)), 6.41 (s, 1H, H(5)), 6.9—7.7 (m, 20H, Ar–H); ^{13}C NMR δ=59.74 (d, C(4)), 68.17 (s, C(2)); MS *m/z* 446 (60, M^+), 414 (41, $M^+{-}S$), 412 (92, $M^+{-}H_2S$), 325 (100, $M^+{-}PhCS$), 324 (70, $M^+{-}PhCHS$); Found: C, 80.53; H, 4.99%. Calcd for $C_{30}H_{22}S_2$: C, 80.71; H, 4.93%.

6′-(*p*-Methoxyphenyl)-2,3,4′-triphenylspiro[2-cyclopropene-1,2′-[4*H*][1,3]dithiin] (14b). ^{1}H NMR δ=3.77 (s, 3H, OCH_3), 5.40 (s, 1H, H(4)), 6.32 (s, 1H, H(5)), 6.7—7.7 (m, 19H, Ar–H); ^{13}C NMR δ=55.31 (q, OCH_3), 59.74 (d, C(4)), 68.22 (s, C(2)); MS *m/z* 476 (66, M^+), 444 (25, $M^+{-}S$), 354 (100, $M^+{-}PhCHS$); Found: C, 78.02; H, 5.11%. Calcd for $C_{31}H_{24}OS_2$: C, 78.15; H, 5.04%.

6′-(*p*-Chlorophenyl)-2,3,4′-triphenylspiro[2-cyclopropene-1,2′-[4*H*][1,3]dithiin] (14c). ^{1}H NMR δ=5.38 (s, 1H, H(4)), 6.38 (s, 1H, H(5)), 6.8—7.7 (m, 19H, Ar–H); ^{13}C NMR δ=59.64 (d, C(4)), 68.13 (s, C(2)); MS *m/z* 480 (51, M^+), 448 (21, $M^+{-}S$), 358 (100, $M^+{-}PhCHS$); Found: C, 74.76; H, 4.21%. Calcd for $C_{30}H_{21}S_2Cl$: C, 74.92; H, 4.37%.

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