Chemistry of α,β-Unsaturated Thione Dimers. 2. Reactions of Thiochalcones and 2-Arylidene-1-thiotetralones with Some Olefins and the Parent Ketones of the Thiones

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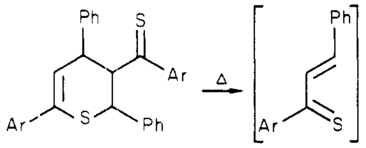
Thiochalcone, 4′-methoxythiochalcone, 2-benzylidene-1-thiotetralone, 2-(*p*-methoxybenzylidene)-1-thiotetralone, and 2-(*p*-chlorobenzylidene)-1-thiotetralone formed by the retro-Diels–Alder reaction of the corresponding dimers reacted with maleic anhydride, citraconic anhydride, styrene, *n*-butyl vinyl ether, norbornene, and norbornadiene to give the [4 + 2] cycloadducts, respectively. These α,β-unsaturated thiones also reacted as a diene with the parent ketones to afford the cycloadducts. Simple qualitative consideration by frontier molecular orbital theory has been made on these cycloaddition reactions.

Hitherto, little attention has been paid to cycloaddition reactions of α,β-unsaturated thiones because of their instability in the monomeric form.[1,7] In our earlier paper dealing with the thermolysis of thiochalcone and 2-arylidene-1-thiotetralone dimers in the presence of acrylonitrile or acrylamide, it was shown that the monomeric α,β-unsaturated thione was generated by retro-Diels–Alder reaction of the dimer.[2]



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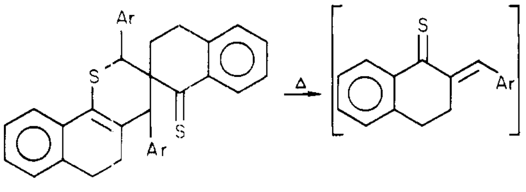

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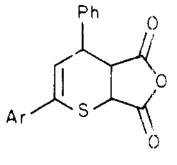
a, Ar = C_6H_5; b, Ar = *p*-$CH_3OC_6H_4$; c, Ar = *p*-ClC_6H_4

The purpose of the present investigation is to describe the results of the reaction of these α,β-unsaturated thiones with olefins and the parent ketones.

Results and Discussion

Thermolysis of **1a** with maleic anhydride gave 1,4-cycloadduct **3a** which had strong IR absorptions due to the anhydride linkage at 1860 and 1790 cm^{-1}. Cycloadduct **4a** obtained by the reaction **2a** and maleic anhydride showed a ^1H NMR in which the coupling between H_a and H_b was 9.0 Hz; this value indicated that the product had a 2,3-cis configuration. Similarly, the reaction of maleic anhydride and thione dimers **1b**, **2b**, or **2c** gave the adducts **3b**, **4b**, or **4c**, respectively (see Table I).



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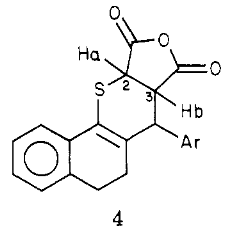

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Table I. Reactions with Maleic Anhydride, Citraconic Anhydride, Styrene, *n*-Butyl Vinyl Ether, Norbornene, and Norbornadiene

product[b]	reaction time, min	mp, °C	yield, %
3a	5	144-146	10[a]
3b	45	161-162	62
4a	16	162-163	56
4b	15	147-147.5	56
4c	40	145-146.5	44
5a	15	144-145	2[a]
6a		158.5-160.5	1[a]
5b	105	138-139	23
7a	30	201-202	43
7b	10	149-150	29
7c	60	162-163	44
8a	3	129	24[a]
8b	15	132-134	48
9a	5	176-178	66
9b	3	143-144	70
9c	8	186-187	72
10a	15		17[a]
10b	25		81
11a	30		90
11b	8		99
11c	20		99
12a	15	140-142	9[a]
12b	30	126-127	65
13a	20	98.5-99.5	72
13b	13	124-125	58
13c	40	153-154	69
14a	5	137-139	2[a]
14b	10	147-148	45
15a	15	104-107	40
15b	8	121-122	41
15c	7	144-146	67

[a] Thiochalcone dimer (synthesized from 10 mmol of chalcone) was obtained as a deep blue syrup and used without crystallization, so the yields were based on chalcone. [b] All the products are colorless crystals (**10** and **11** are pale yellow oils).

Thermolysis of **1** or **2** with citraconic anhydride gave the adducts **5** or **7**, respectively. Only in the case of **1a** was a small amount of the regioisomer **6a** isolated. The structures of **5a** (Ar = C_6H_5) and **6a** could easily and unequiv-

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(1) D. C. Sen, *J. Indian Chem. Soc.*, **13**, 268 (1936); D. A. Winkler and S. A. Ballard, U.S. Patent 2 443 811 (1948); R. Bourdon, *Bull. Soc. Chim. Fr.*, 722 (1958); F. A. King, *Chem. Ber.*, **93**, 1043 (1960); Y. Kitahara and M. Funamizu, *Bull. Chem. Soc. Jpn.*, **37**, 1897 (1964); T. Eicher and G. Frenzel, *Z. Naturforsch.*, **20**, 274 (1965); P. Metzner and J. Vialle, *Bull. Soc. Chim. Fr.*, 3739 (1970); H. Hartmann and R. Mayer, *D.D.R. Patent* 73 753, (1971); *Chem. Abstr.*, **71**, 53 302 (1971); P. Metzner, *Bull. Soc. Chim. Fr.*, 3138 (1972); J. P. Pradere, G. Bouet, and H. Quiniou, *Tetrahedron Lett.*, 3471 (1972); G. Jacqmin, J. Nasielsky, G. Gilly, and M. Remy, *ibid.*, 3655 (1973); A. G. Hortmann, A. J. Aron, and A. K. Bhattacharya, *J. Org. Chem.*, **43**, 3374 (1978).

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

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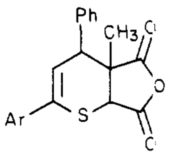
ocally be distinguished on the basis of the ^{1}H NMR spectra.



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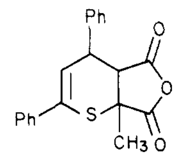
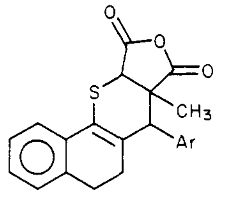


6a



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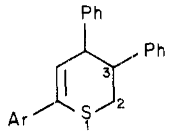
The reaction of **1** or **2** with styrene gave the adducts **8** or **9**, respectively, which showed multiplets of methylene protons at 3.00–3.67 ppm in their ^{1}H NMR spectra. These signals are assigned to the C-2 gem AB protons in **8** or **9**.[3]



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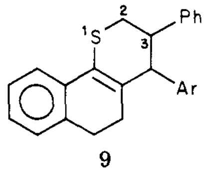

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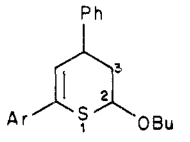
Cycloaddition of **1a** and *n*-butyl vinyl ether gave the adduct **10a**. Although the product could not be purified



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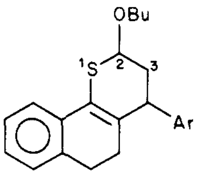

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by distillation or crystallization, its mass spectrum showed mol wt 324, an ion peak at *m/e* 224 for thiochalcone, and the characteristic thiopyrrylium ion peak at *m/e* 223.[2] In the ^{1}H NMR, the resonance at 5.26 ppm is assigned to the methine proton (>CHOR) while the multiplet at 2.00–2.66 ppm is attributed to the C-3 AB protons by spin decoupling. Reactions with the other thione dimers **1b**–**2c** afforded the corresponding adducts **10b**–**11c**, respectively.

Thermolysis of **1a** with norbornene gave the adduct **12a**. The configuration of the product was determined by ^{13}C NMR spectroscopy. The noise-decoupled ^{13}C spectrum of **12a** showed the expected 17 sharp lines. The most upfield signals that appeared in the off-resonance decoupled spectrum were as follows: (1) a triplet at 29.14 ppm, (2) a triplet at 29.77 ppm, (3) a double doublet at 34.01 ppm. The first and the second signals correspond to the C-5 and C-6 methylene carbons, respectively. The third resonance is a methylene carbon which is attached to the protons having widely separated chemical shifts[4] and thus identified as the absorption due to C-7. A substituent effect on the ^{13}C NMR in the norbornyl ring system has been reported by some workers.[5] In the case of 2-substituted norbornane, the exo-2 group usually shields C-7 (the resonance of C-7 is upfield 1.3–4.4 ppm from the one in norbornane) while its endo counterpart shields C-6 (the resonance of C-6 is upfield 4.9–9.7 ppm from the one in norbornane). The C-7 resonance of **12a** is shifted upfield 4.69 ppm and those of C-5 and C-6 are shifted upfield 0.96 and 0.33 ppm in comparison with those of norbornane; these values indicated that **12a** had the cis-exo configuration. Similarly, cycloadducts of **12b**, **13a**, **13b**, and **13c** were obtained and their structures were assigned by spectral and analytical data.

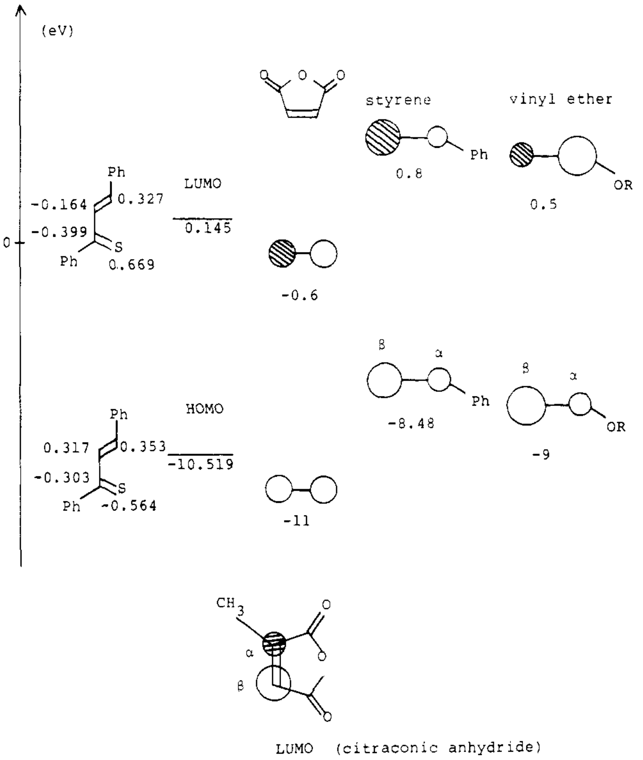
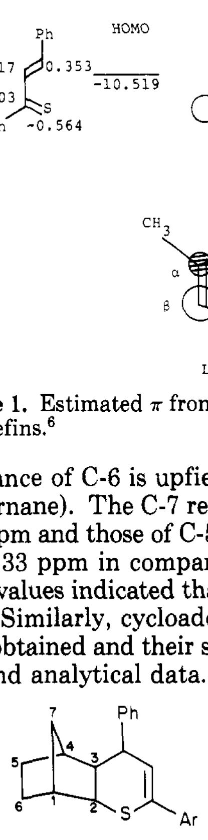


Figure 1. Estimated π frontier orbital energies of thiochalcone and olefins.[6]



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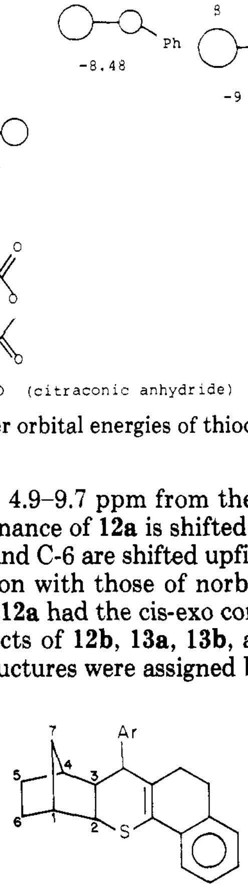

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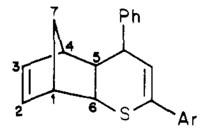
Thermolysis of **1a** with norbornadiene gave the adduct **14a**. The elementary analysis and mass spectrum were in agreement with the 1:1 adduct. The ^{1}H NMR showed two methine protons at 2.08 and 3.28 ppm corresponding to H-5 and H-6, respectively. The coupling between H-5 and H-6 was 8.0 Hz; this value indicated the cis configuration. The noise-decoupled ^{13}C spectrum of **14a** showed the 17 sharp lines. The most upfield signal that appeared in the off-resonance decoupled spectrum was a double doublet at 43.66 ppm. This signal corresponded to the C-7 methylene carbon which shifted upfield 5.1 ppm in comparison with that of norbornene; this value indicated the exo configuration.



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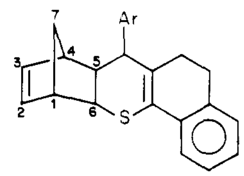

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Frontier molecular orbital theory (FMO) has provided a basis for explaining a wide variety of the aspects of the

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(3) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1969; see ref 2.

(4) E. Wenkert, D. W. Cochron, E. W. Hagaman, F. M. Schell, N. Neuso, A. S. Katner, P. Potier, C. Kan, M. Plat, M. Koch, H. Mehri, J. Poisson, N. Kunesch, and Y. Rolland, *J. Am. Chem. Soc.*, **95**, 4990 (1973).

(5) N. K. Wilson and J. B. Stothers, *Top. Stereochem.*, 8, 1 (1974); J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972; G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, 1972. In the case of **12** and **13**, the configuration could not be determined by ^{1}H NMR because of the difficulty in the assignment of the H-2 and H-3 signals.

Table II. Reactions of the α,β-Unsaturated Thiones with the Parent Ketones

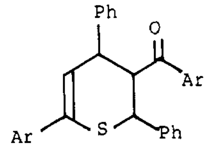
product	reaction time, h	mp, °C	yield, %	IR $\nu_{C=O}$, cm^{-1}
16a	1	187.5-188.5	28	1695
17a		143.5-144.5	54	1680
16b **17b**	2	*a*	51	1680 (br)[b]
18a **19a**	7	*c*	59	1680 (br)[b]
18b	10	211-212	28	1690
19b		176-178	17	1680
18c	7	237-237.5	23	1695
19c		213-214	68	1690

[a] Yellow powder, mixture of the regioisomers. [b] Broad band. [c] Colorless solid, mixture of the regioisomers.

1,4-cycloaddition reaction.[6] With this theory, some of the qualitative observations on the results of the preceding reactions can be correlated. The CNDO/2 calculations of the FMO of thiochalcone are given in Figure 1. As can be seen from the figure, stabilization of the transition state would result predominantly from the HOMO(thiochalcone)-LUMO(olefin) interaction in the case of the reaction with maleic anhydride and from the LUMO(thiochalcone)-HOMO(olefin) interaction in the case of styrene and *n*-butyl vinyl ether. The energy separation of the FMO between thiochalcone and the olefins increases in the order of styrene < *n*-butyl vinyl ether < maleic anhydride, and the actual reactivity of the olefins toward the thione was found to increase in the order of styrene > *n*-butyl vinyl ether > maleic anhydride, qualitatively. Though the reactions with the unsymmetric olefins can afford regioisomers, only one regioisomer was obtained, except in the case of citraconic anhydride. The largest LUMO coefficient of citraconic anhydride is at the β carbon atom, which should become linked to the sulfur atom, the site of the largest HOMO coefficient of thiochalcone. In the case of styrene, the largest HOMO coefficient of styrene is at the β carbon atom, which should become linked to the largest LUMO coefficient of thiochalcone. This prediction of the regioselectivity is in fair agreement with the experimental results. However, in the case of *n*-butyl vinyl ether, the regioselectivity was opposite to that expected from the FMO. This suggests that the contribution from the ground-state polarization of thiochalcone and *n*-butyl vinyl ether is more important than that from the orbital interaction.

Both the α,β-unsaturated thione and the parent ketone may serve as a diene or dienophile in cycloaddition reactions. When **1a** was allowed to react with chalcone, regioisomeric products **16a** and **17a** were obtained. Similarly, the reactions of **1b**, **2a**, **2b**, or **2c** with the parent ketone gave a pair of two regioisomers (see Table II). Separation of the isomers obtained from **1b** and **2a** were unsuccessful. Although formation of **16** and **18** undoubtedly indicates that the thione reacted as a diene, two possible paths can be considered for the formation of **17** and **19**.

One is that the thione **20** served as a diene, and another is that the ketone **21** served as a diene, and the resulting adduct **22** underwent [3,3] sigmatropic rearrangement[7] to give **23**. When the reaction of **2a** and 2-benzylidene-1-tetralone was carried out in deuteriochloroform and monitored by ^1H NMR, any absorptions other than those of **2a**, **18a**, and **19a** could not be observed. Therefore, it has been found that the thione also behaved as a diene in this case.



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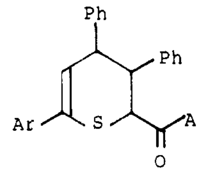

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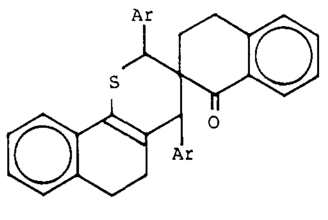

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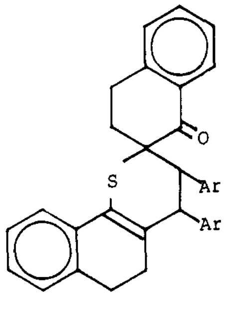

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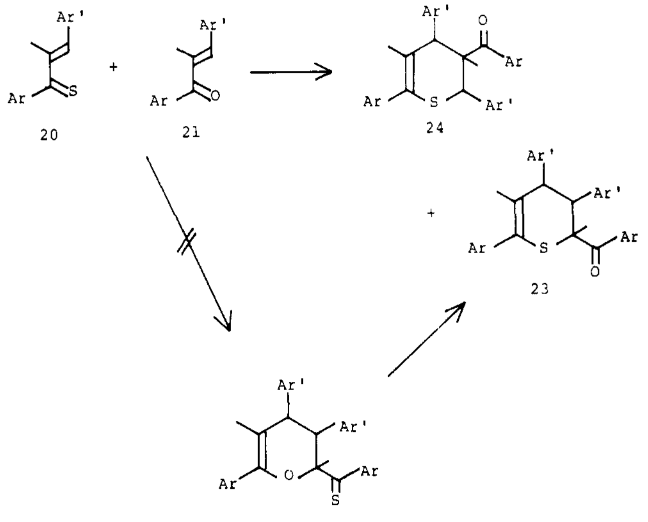

Experimental Section

All the melting points are uncorrected. ^1H NMR spectra were recorded at 60 MHz on a JEOL JNM-PMX 60 spectrometer and at 100 MHz on a JEOL JNM-FX 100 spectrometer using Me_4Si as internal standard. ^{13}C NMR spectra were recorded at 25 MHz on a JEOL JNM-FX 100 spectrometer using Me_4Si as internal standard. IR spectra were obtained on an Hitachi Model 260-10 infrared spectrometer. Mass spectral data were obtained with an Hitachi double-focusing mass spectrometer, Model RMU-7M. Thiochalcone, 4′-methoxythiochalcone, 2-benzylidene-1-thiotetralone, 2-(*p*-methoxybenzylidene)-1-thiotetralone, and 2-(*p*-chlorobenzylidene)-1-thiotetralone dimers were prepared and

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(6) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", Wiley, London, 1976; K. Fukui, "Kagaku-hannoh To Denshi No Kidoh", Maruzen, Tokyo, 1976; G. Desimoni and G. Tacconi, *Chem. Rev.*, **75**, 651 (1975); K. N. Houk, "Pericyclic Reactions", A. P. Marchand and R. E. Lehr, Ed., Vol. II, Academic Press, New York, p 181, 1977.

(7) K. B. Lipkowitz and B. P. Mundy, *Tetrahedron Lett.*, 3417 (1977); K. B. Lipkowitz, S. Scarpone, B. P. Mundy, and W. G. Bornmann, *J. Org. Chem.*, **44**, 486 (1979).

purified according to the method described previously.[2]

Typical Procedure for the Reactions of 1a with Maleic Anhydride, Citraconic Anhydride, Styrene, *n*-Butyl Vinyl Ether, Norbornene, and Norbornadiene. Thiochalcone dimer (synthesized from 10 mmol of chalcone) was obtained as a deep blue syrup and used without crystallization. A suspension of thiochalcone dimer and maleic anhydride (0.33 g) in dry benzene (8 mL) was gently refluxed for 5 min under a nitrogen atmosphere. The benzene was removed, and the residue was chromatographed on Wakogel C-200 with benzene–hexane (7:3) as the eluent. The solvent was evaporated, and the residue was recrystallized from ligroin to give **4,6-diphenyl-3,4-dihydro-2*H*-thiopyran-2,3-dicarboxylic anhydride (3a)**: MS (70 eV) *m/e* 322 (M^+, 14), 224 (72), 223 (100); IR (Nujol) 1860 and 1790 cm^{-1} (C═O); NMR ($CDCl_3$) δ 3.80–4.40 (m, 3 H), 6.73 (t, 1 H), 7.17–7.63 (m, 10 H). Anal. Calcd for $C_{19}H_{14}O_3S$: C, 70.79; H, 4.38; S, 9.94. Found: C, 70.62; H, 4.25; S, 9.83.

3-Methyl-4,6-diphenyl-3,4-dihydro-2*H*-thiopyran-2,3-dicarboxylic anhydride (5a): chromatographed on Wakogel C-200 with hexane–benzene (1:1); MS (70 eV) *m/e* 336 (M^+, 2), 224 (70), 223 (100); IR (Nujol) 1860 and 1785 cm^{-1} (C═O); NMR ($CDCl_3$) δ 1.50 (s, 3 H), 3.47 (d, 1 H, J = 5.0 Hz), 4.02 (s, 1 H), 6.57 (d, 1 H, J = 5.0 Hz), 7.13–7.62 (m, 10 H). Anal. Calcd for $C_{20}H_{16}O_3S$: C, 71.41; H, 4.79; S, 9.53. Found: C, 71.54; H, 4.84; S, 9.64.

2-Methyl-4,6-diphenyl-3,4-dihydro-2*H*-thiopyran-2,3-dicarboxylic anhydride (6a): MS (70 eV) *m/e* 336 (M^+, 10), 224 (64), 223 (100); IR (Nujol) 1850 and 1780 cm^{-1} (C═O); NMR ($CDCl_3$) δ 1.87 (s, 3 H), 3.67–3.80 (m, 2 H), 6.75 (d, 1 H, J = 4.0 Hz), 7.17–7.67 (m, 10 H). Anal. Calcd for $C_{20}H_{16}O_3S$: C, 71.41; H, 4.79; S, 9.53. Found: C, 71.44; H, 4.93; S, 9.65.

3,4,6-Triphenyl-3,4-dihydro-2*H*-thiopyran (8a): recrystallized from ethanol; MS (70 eV) *m/e* 328 (M^+, 15), 224 (75), 223 (100); NMR ($CDCl_3$) δ 2.66–2.82 (m, 1 H), 3.25–3.64 (m, 2 H), 3.81 (dd, 1 H, J = 1.6 and 6.4 Hz), 6.22 (d, 1 H, J = 6.4 Hz), 6.61–7.62 (m, 15 H). Anal. Calcd for $C_{23}H_{20}S$: C, 84.10; H, 6.13; S, 9.76. Found: C, 83.77; H, 6.27; S, 9.63.

2-Butoxy-4,6-diphenyl-3,4-dihydro-2*H*-thiopyran (10a): chromatographed on Wakogel C-200 with benzene–ligroin (1:1); MS (70 eV) *m/e* 324 (M^+, 8), 251 (20), 250 (100), 224 (12), 223 (50); NMR ($CDCl_3$) δ 0.83–1.00 (m, 3 H), 1.16–1.70 (m, 4 H), 2.00–2.66 (m, 2 H), 3.38–4.02 (m, 3 H), 5.26 (q, 1 H, J = 4.0 and 8.0 Hz), 6.08 (d, 1 H, J = 4.0 Hz), 7.20–7.60 (m, 10 H). Calcd for $C_{21}H_{24}OS$ (M), *m/e* 324.1548; found, *m/e* 324.1544.

***exo*-4,6-Diphenyl-3-thiatricyclo[6.2.1.0^{2,7}]undec-4-ene (12a)**: recrystallized from ethanol; MS (70 eV) *m/e* 318 (M^+, 49), 224 (67), 223 (100); NMR ($CDCl_3$) δ 1.00–2.33 (m, 9 H), 3.00–3.27 (m, 2 H), 6.37 (d, 1 H, J = 4.0 Hz), 7.03–7.63 (m, 10 H). Anal. Calcd for $C_{22}H_{22}S$: C, 82.97; H, 6.96; S, 10.07. Found: C, 82.73; H, 6.85; S, 10.10.

***exo*-4,6-Diphenyl-3-thiatricyclo[6.2.1.0^{2,7}]undeca-4,9-diene (14a)**: recrystallized from hexane; MS (70 eV) *m/e* 316 (M^+, 6), 250 (100), 173 (56); NMR ($CDCl_3$) δ 1.60 (m, 1 H), 2.10 (m, 1 H, J = 13.0, 8.0, and 2.0 Hz), 2.56 (m, 1 H), 2.60 (m, 1 H), 2.92 (m, 1 H), 3.30 (dd, 1 H, J = 8.0 and 2.0 Hz), 3.38 (dd, 1 H, J = 13.0 and 4.0 Hz), 6.00 (m, 2 H), 6.58 (d, 1 H, J = 4.0 Hz), 7.21–7.64 (m, 10 H). Anal. Calcd for $C_{22}H_{20}S$: C, 83.50; H, 6.37; S, 10.13. Found: C, 83.31; H, 6.80; S, 10.22.

Typical Procedure for the Reactions of 1b–2c with Styrene, *n*-Butyl Vinyl Ether, and Norbornadiene. A suspension of 4′-methoxythiochalcone dimer (0.714 g, 1.5 mmol) in styrene (8 mL) was gently refluxed for 15 min under a nitrogen atmosphere. The excess styrene was removed, and recrystallization of the residue from ethanol gave **6-(*p*-methoxyphenyl)-3,4-diphenyl-3,4-dihydro-2*H*-thiopyran (8b)**: MS (70 eV) *m/e* 358 (M^+, 11), 254 (91), 253 (100); NMR ($CDCl_3$) δ 2.73–2.90 (m, 1 H), 3.03–3.60 (m, 2 H), 3.73–3.90 (1 H), 3.83 (s, 3 H), 6.20 (d, 1 H, J = 6.0 Hz), 6.63–7.63 (m, 14 H). Anal. Calcd for $C_{24}H_{22}OS$: C, 80.41; H, 6.18. Found: C, 80.39; H, 6.34.

3,4-Diphenyl-5,6-dihydrobenzo[*h*]thiochroman (9a): recrystallized from ethanol; MS (70 eV) *m/e* 354 (M^+, 24), 250 (61), 249 (100); NMR ($CDCl_3$) δ 2.00–2.85 (m, 5 H), 3.00–3.58 (m, 2 H), 3.58 (1 H), 6.50–7.67 (m, 14 H). Anal. Calcd for $C_{25}H_{22}S$: C, 84.70; H, 6.26. Found: C, 85.16; H, 6.26.

3-(*p*-Methoxyphenyl)-4-phenyl-5,6-dihydrobenzo[*h*]thiochroman (9b): recrystallized from ethanol; MS (70 eV) *m/e* 384 (M^+, 24), 280 (100), 279 (99), 265 (40), 249 (80); NMR ($CDCl_3$) δ 2.00–2.83 (m, 5 H), 3.00–3.53 (m, 2 H), 3.53 (1 H), 3.71 (s, 3 H), 6.57–7.60 (m, 13 H). Anal. Calcd for $C_{26}H_{24}OS$: C, 81.21; H, 6.29. Found: C, 81.27; H, 6.34.

3-(*p*-Chlorophenyl)-4-phenyl-5,6-dihydrobenzo[*h*]thiochroman (9c): recrystallized from ethanol; MS (70 eV) *m/e* 388 (M^+, 28), 284 (74), 283 (93), 249 (100); NMR ($CDCl_3$) δ 2.00–2.93 (m, 5 H), 3.00–3.50 (m, 2 H), 3.50 (1 H), 6.60–7.60 (m, 13 H). Anal. Calcd for $C_{25}H_{21}ClS$: C, 77.20; H, 5.44. Found: C, 77.26; H, 5.70.

2-Butoxy-6-(*p*-methoxyphenyl)-4-phenyl-3,4-dihydro-2*H*-thiopyran (10b): chromatographed on Wakogel C-200 with benzene; MS (70 eV) *m/e* 354 (M^+, 22), 281 (25), 280 (100), 254 (27), 253 (71); NMR ($CDCl_3$) δ 0.80–1.00 (m, 3 H), 1.16–1.68 (m, 4 H), 2.04–2.64 (m, 2 H), 3.36–3.92 (m, 3 H), 3.76 (s, 3 H), 5.23 (q, 1 H, J = 9.0 and 4.0 Hz), 5.98 (d, 1 H, J = 4.0 Hz), 6.80–7.52 (m, 9 H).

2-Butoxy-4-phenyl-5,6-dihydrobenzo[*h*]thiochroman (11a): chromatographed on Wakogel C-200 using benzene; MS (70 eV) *m/e* 350 (M^+, 32), 277 (25), 276 (100), 250 (17), 249 (54); NMR ($CDCl_3$) δ 0.76–0.90 (m, 3 H), 1.04–1.56 (m, 4 H), 1.96–2.12 (m, 2 H), 2.40–2.75 (m, 4 H), 3.14–3.88 (m, 3 H), 5.05 (q, 1 H, J = 7.0 and 4.0 Hz), 7.05–7.56 (m, 9 H).

2-Butoxy-4-(*p*-methoxyphenyl)-5,6-dihydrobenzo[*h*]thiochroman (11b): chromatographed on Wakogel C-200 with chloroform; MS (70 eV) *m/e* 380 (M^+, 42), 307 (26), 306 (100), 280 (17), 279 (43), 265 (17), 249 (27); NMR ($CDCl_3$) δ 0.80–0.97 (m, 3 H), 1.17–1.57 (m, 4 H), 1.87–2.17 (m, 2 H), 2.30–2.80 (m, 4 H), 3.07–3.84 (m, 3 H), 3.72 (s, 3 H), 5.02 (q, 1 H, J = 6.0 and 4.0 Hz), 6.63–7.60 (m, 8 H).

2-Butoxy-4-(*p*-chlorophenyl)-5,6-dihydrobenzo[*h*]thiochroman (11c): chromatographed on Wakogel C-200 with benzene; MS (70 eV) *m/e* 384 (M^+, 24), 311 (29), 310 (100), 284 (11), 283 (32), 249 (33); NMR ($CDCl_3$) δ 0.76–0.88 (m, 3 H), 1.06–1.45 (m, 4 H), 1.98–2.12 (m, 2 H), 2.40–2.76 (m, 4 H), 3.16–3.85 (m, 3 H), 5.02 (q, 1 H, J = 7.0 and 4.0 Hz), 7.08–7.56 (m, 8 H).

***exo*-4-(*p*-Methoxyphenyl)-6-phenyl-3-thiatricyclo[6.2.1.0^{2,7}]undeca-4,9-diene (14b)**: recrystallized from ethanol; MS (70 eV) *m/e* 346 (M^+, 11), 280 (100), 279 (21), 203 (44); NMR ($CDCl_3$) δ 1.58 (m, 1 H), 2.08 (m, 1 H, J = 13.0, 8.0, and 2.0 Hz), 2.56 (m, 1 H), 2.58 (m, 1 H), 2.91 (m, 1 H), 3.28 (dd, 1 H, J = 8.0 and 2.0 Hz), 3.34 (dd, 1 H, J = 13.0 and 4.0 Hz), 3.76 (s, 3 H), 6.08 (m, 2 H), 6.44 (d, 1 H, J = 4.0 Hz), 6.77–7.56 (m, 9 H). Anal. Calcd for $C_{23}H_{22}OS$: C, 79.73; H, 6.40. Found: C, 80.12; H, 6.49.

***exo*-10-Phenylbenz[*c*]-3-thiatetracyclo[10.2.1.0^{2,11}.0^{4,9}]hexadeca-4,13-diene (15a)**: chromatographed on Wakogel C-200 with hexane–benzene (1:1); MS (70 eV) *m/e* 342 (M^+, 10), 276 (86), 199 (100); NMR ($CDCl_3$) δ 1.52 (m, 1 H), 1.68–2.68 (m, 7 H), 2.90 (m, 1 H), 3.18 (dd, 1 H, J = 8.0 and 2.0 Hz), 3.78 (d, 1 H, J = 11.0 Hz), 6.08 (m, 2 H), 6.95–7.70 (m, 9 H). Anal. Calcd for $C_{24}H_{22}S$: C, 84.17; H, 6.47. Found: C, 84.51; H, 6.10.

***exo*-10-(*p*-Methoxyphenyl)benz[*c*]-3-thiatetracyclo[10.2.1.0^{2,11}.0^{4,7}]hexadeca-4,13-diene (15b)**: recrystallized from ethanol; MS (70 eV) *m/e* 372 (M^+, 10), 306 (100), 199 (45); NMR ($CDCl_3$) δ 1.50 (m, 1 H), 1.75–2.75 (m, 7 H), 2.87 (m, 1 H), 3.17 (dd, 1 H, J = 9.0 and 2.0 Hz), 3.68 (1 H), 3.77 (s, 3 H), 6.07 (m, 2 H), 6.73–7.67 (m, 8 H). Anal. Calcd for $C_{25}H_{24}OS$: C, 80.61; H, 6.49. Found: C, 80.89; H, 6.59.

***exo*-10-(*p*-Chlorophenyl)benz[*c*]-3-thiatetracyclo[10.2.1.0^{2,11}.0^{4,9}]hexadeca-4,13-diene (15c)**: recrystallized from ethanol; MS (70 eV) *m/e* 376 (M^+, 8), 310 (96), 199 (100); NMR ($CDCl_3$) δ 1.53 (m, 1 H), 1.68–2.70 (m, 7 H), 2.90 (m, 1 H), 3.18 (dd, 1 H, J = 9.0 and 2.0 Hz), 3.74 (d, 1 H, J = 11.0 Hz), 6.09 (m, 2 H), 7.00–7.67 (m, 8 H). Anal. Calcd for $C_{24}H_{21}ClS$: C, 76.47; H, 5.61. Found: C, 76.70; H, 5.78.

Typical Procedure for the Reactions of 1b–2c with Maleic Anhydride, Citraconic Anhydride, and Norbornene. A solution of 4′-methoxythiochalcone dimer (0.762 g, 1.5 mmol) and maleic anhydride (0.294 g, 3 mmol) in dry benzene (8 mL) was gently refluxed for 45 min under a nitrogen atmosphere. The benzene was removed, and recrystallization of the residue from benzene–ligroin gave **6-(*p*-methoxyphenyl)-4-phenyl-3,4-dihydro-2*H*-thiopyran-2,3-dicarboxylic anhydride (3b)**: MS (70 eV) *m/e* 352 (M^+, 23), 254 (71), 253 (100); IR (Nujol) 1855 and 1780 cm^{-1} (C═O); NMR ($CDCl_3$) δ 3.81 (s, 3 H), 3.63–4.50 (m, 3 H), 6.70 (d, 1 H, J = 4.0 Hz), 6.81–7.60 (m, 9 H). Anal. Calcd for $C_{20}H_{16}O_4S$: C, 68.17; H, 4.58 Found: C, 67.88; H, 4.67.

4-Phenyl-5,6-dihydrobenzo[*h*]thiochroman-2,3-di-

carboxylic anhydride (4a): recrystallized from ligroin–benzene; MS (70 eV) *m/e* 348 (M^+, 48), 250 (38), 249 (100); IR (Nujol) 1865 and 1790 cm^{-1} (C=O); NMR ($CDCl_3$) δ 2.06–2.90 (m, 4 H), 4.03 (d, 1 H, J = 9.0 and $\sim$0 Hz), 4.10 (s, 1 H, $J \simeq 0$ Hz), 4.46 (d, 1 H, J = 9.0 Hz), 7.00–7.67 (m, 9 H). Anal. Calcd for $C_{21}H_{16}O_3S$: C, 72.39; H, 4.63. Found: C, 72.35; H, 4.78.

4-(*p*-Methoxyphenyl)-5,6-dihydrobenzo[*h*]thiochroman-2,3-dicarboxylic anhydride (4b): recrystallized from ligroin–benzene; MS (70 eV) *m/e* 378 (M^+, 60), 280 (71), 279 (100); IR (Nujol) 1860, 1840, and 1780 cm^{-1} (C=O); NMR ($CDCl_3$) δ 2.13–2.88 (m, 4 H), 3.81 (s, 3 H), 3.96 (d, 1 H, J = 9.0 and $\sim$0 Hz), 4.03 (s, 1 H, $J \simeq 0$ Hz), 4.50 (d, 1 H, J = 9.0 Hz), 6.81–7.51 (m, 8 H). Anal. Calcd for $C_{22}H_{18}O_4S$: C, 69.82; H, 4.79. Found: C, 69.74; H, 4.87.

4-(*p*-Chlorophenyl)-5,6-dihydrobenzo[*h*]thiochroman-2,3-dicarboxylic anhydride (4c): recrystallized from ligroin–benzene; MS (70 eV) *m/e* 382 (M^+, 52), 283 (97), 249 (100); IR (Nujol) 1860 and 1790 cm^{-1} (C=O); NMR ($CDCl_3$) δ 2.06–2.86 (m, 4 H), 4.01 (d, 1 H, J = 9.0 Hz), 4.06 (s, 1 H, $J \simeq 0$ Hz), 4.46 (d, 1 H, J = 9.0 Hz), 7.03–7.58 (m, 8 H). Anal. Calcd for $C_{21}H_{15}ClO_3S$: C, 65.88; H, 3.95. Found: C, 66.01; H, 4.18.

3-Methyl-6-(*p*-methoxyphenyl)-4-phenyl-3,4-dihydro-2*H*-thiopyran-2,3-dicarboxylic anhydride (5b): recrystallized from ligroin–benzene; MS (70 eV) *m/e* 366 (M^+, 4), 254 (78), 253 (100); IR (Nujol) 1860 and 1780 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.47 (s, 3 H), 3.47 (d, 1 H, J = 5.0 Hz), 3.73 (s, 3 H), 3.98 (s, 1 H), 6.47 (d, 1 H, J = 5.0 Hz), 6.70–7.67 (m, 9 H). Anal. Calcd for $C_{21}H_{18}O_4S$: C, 68.83; H, 4.95. Found: C, 69.22; H, 5.00.

3-Methyl-4-phenyl-5,6-dihydrobenzo[*h*]thiochroman-2,3-dicarboxylic anhydride (7a): recrystallized from ligroin–benzene; MS (70 eV) *m/e* 362 (M^+), 250 (38), 249 (15); IR (Nujol) 1870 and 1790 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.57 (s, 3 H), 2.17–2.93 (m, 4 H), 3.63 (s, 1 H), 4.13 (s, 1 H), 7.10–7.73 (m, 9 H). Anal. Calcd for $C_{22}H_{18}O_3S$: C, 72.91; H, 5.01. Found: C, 72.82; H, 5.15.

3-Methyl-4-(*p*-methoxyphenyl)-5,6-dihydrobenzo[*h*]thiochroman-2,3-dicarboxylic anhydride (7b): recrystallized from ligroin–benzene; MS (70 eV) *m/e* 392 (M^+, 20), 280 (87), 279 (100), 265 (42), 249 (70); IR (Nujol) 1870 and 1790 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.55 (s, 3 H), 2.15–2.91 (m, 4 H), 3.58 (s, 1 H), 3.73 (s, 3 H), 4.13 (s, 1 H), 6.83–7.83 (m, 8 H). Anal. Calcd for $C_{23}H_{20}O_4S$: C, 70.39; H, 5.14. Found: C, 70.27; H, 4.89.

4-(*p*-Chlorophenyl)-3-methyl-5,6-dihydrobenzo[*h*]thiochroman-2,3-dicarboxylic anhydride (7c): recrystallized from ligroin–benzene; MS (70 eV) *m/e* 396 (M^+, 19), 284 (72), 283 (92), 249 (100); IR (Nujol) 1860 and 1780 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.53 (s, 3 H), 2.10–2.93 (m, 4 H), 3.63 (s, 1 H), 4.16 (s, 1 H), 7.06–7.80 (m, 8 H). Anal. Calcd for $C_{22}H_{17}ClO_3S$: C, 66.60; H, 4.32. Found: C, 66.47; H, 4.53.

***exo*-4-(*p*-Methoxyphenyl)-6-phenyl-3-thiatricyclo[6.2.1.0^{2,7}]undec-4-ene (12b)**: recrystallized from ethanol; MS (70 eV) *m/e* 348 (M^+, 40), 254 (86), 253 (100); NMR ($CDCl_3$) δ 1.07–2.33 (m, 9 H), 3.00–3.27 (m, 2 H), 3.70 (s, 3 H), 6.33 (d, 1 H, J = 4.0 Hz), 6.70–7.57 (m, 9 H). Anal. Calcd for $C_{23}H_{24}OS$: C, 79.27; H, 6.94. Found: C, 79.14; H, 6.83.

***exo*-10-Phenylbenz[*c*]-3-thiatetracyclo[10.2.1.0^{2,11}.0^{4,9}]hexadec-4-ene (13a)**: recrystallized from ethanol; MS (70 eV) *m/e* 344 (M^+, 59), 250 (54), 249 (100); NMR ($CDCl_3$) δ 1.00–2.77 (m, 13 H), 3.00–3.70 (m, 2 H), 6.93–7.73 (m, 9 H). Anal. Calcd for $C_{24}H_{24}S$: C, 83.67; H, 7.02. Found: C, 83.67; H, 7.09.

***exo*-10-(*p*-Methoxyphenyl)benzo[*c*]-3-thiatetracyclo[10.2.1.0^{2,11}.0^{4,9}]hexadec-4-ene (13b)**: recrystallized from ethanol; MS (70 eV) *m/e* 374 (M^-, 93), 280 (85), 279 (100), 265 (38), 249 (82); NMR ($CDCl_3$) δ 1.00–2.77 (m, 13 H), 3.00–3.63 (m, 2 H), 3.77 (s, 3 H), 6.60–7.70 (m, 8 H). Anal. Calcd for $C_{25}H_{26}OS$: C, 80.17; H, 7.00. Found: C, 80.00; H, 7.22.

***exo*-10-(*p*-Chlorophenyl)benzo[*c*]-3-thiatetracyclo[10.2.1.0^{2,11}.0^{4,9}]hexadec-4-ene (13c)**: recrystallized from ethanol; MS (70 eV) *m/e* 378 (M^+, 86), 284 (73), 283 (88), 249 (100); NMR ($CDCl_3$) δ 1.07–2.77 (m, 13 H), 3.00–3.67 (m, 2 H), 6.90–7.67 (m, 8 H). Anal. Calcd for $C_{24}H_{23}ClS$: C, 76.07; H, 6.12. Found: C, 76.16; H, 6.01.

Typical Procedure for the Reactions of the α,β-Unsaturated Thiones with the Parent Ketones. A solution of thiochalcone dimer (0.224 g, 0.5 mmol) and chalcone (0.208 g, 1 mmol) in dry benzene (2 mL) was gently refluxed for 1 h under a nitrogen atmosphere. The benzene was removed and the residue was chromatographed on Wakogel C-200 with benzene–hexane (7:3) as the eluent.

3-Benzoyl-2,4,6-triphenyl-3,4-dihydro-2*H*-thiopyran (16a): MS (70 eV) *m/e* 432 (M^+, 3), 224 (69), 223 (100); NMR ($CDCl_3$) δ 4.20 (dd, 1 H, J = 6.4 and 3.6 Hz), 4.72 (d, 1 H, J = 3.6 and $\sim$0 Hz), 4.78 (s, 1 H, $J \simeq 0$ Hz), 6.30 (d, 1 H, J = 6.4 Hz), 6.87–7.93 (m, 20 H). Anal. Calcd for $C_{30}H_{24}OS$: C, 83.33; H, 5.59; S, 7.42. Found: C, 83.40; H, 5.71; S, 7.50.

2-Benzoyl-3,4,6-triphenyl-3,4-dihydro-2*H*-thiopyran (17a): MS (70 eV) *m/e* 432 (M^+, 3), 224 (46), 223 (100); NMR ($CDCl_3$) δ 3.70–4.17 (m, 2 H), 5.20–5.50 (m, 1 H), 6.27–6.40 (q, 1 H), 6.57–7.93 (m, 20 H). Anal. Calcd for $C_{30}H_{24}OS$: C, 83.33; H, 5.59. Found: C, 83.20; H, 5.50.

Mixture of **16b** and **17b**: chromatographed on Cicagel with benzene–hexane (1:1); NMR ($CDCl_3$) δ 3.56 (s), 3.63 (s), 4.67 (m), 5.20–5.50 (m). Anal. Calcd for $C_{32}H_{28}O_3S$: C, 78.02; H, 5.73. Found: C, 77.99; H, 6.08.

Mixture of **18a** and **19a**: recrystallized from ethanol; NMR ($CDCl_3$) δ 2.00–3.00 (m), 3.80 (s), 3.92 (d, J = 11.0 Hz), 4.58 (d, J = 11.0 Hz), 5.37 (s), 7.00–7.95 (m). Anal. Calcd for $C_{34}H_{28}OS$: C, 84.26; H, 5.82. Found: C, 84.44; H, 5.85.

18b: fractional recrystallization; MS (70 eV) *m/e* 544 (M^+, 4), 280 (56), 279 (70), 264 (83), 263 (100); NMR ($CDCl_3$) δ 2.00–3.17 (m, 8 H), 3.65 (s, 1 H), 3.67 (s, 3 H), 3.75 (s, 3 H), 5.28 (s, 1 H), 6.50–7.90 (m, 16 H). Anal. Calcd for $C_{36}H_{32}O_3S$: C, 79.38; H, 5.92. Found: C, 79.55; H, 6.15.

19b: MS (70 eV) *m/e* 544 (M^+, 7), 280 (87), 279 (100), 264 (39), 263 (47); NMR ($CDCl_3$) δ 2.00–2.85 (m, 8 H), 3.60 (s, 3 H), 3.61 (s, 3 H), 3.80 (d, 1 H, J = 11.0 Hz), 4.50 (d, 1 H, J = 11.0 Hz), 6.50–7.93 (m, 16 H). Anal. Calcd for $C_{36}H_{32}O_3S$: C, 79.38; H, 5.92. Found: C, 79.54; H, 6.18.

18c: fractional recrystallization; MS (70 eV) *m/e* 554 (M^+, 8), 284 (99), 283 (100), 249 (96). Anal. Calcd for $C_{34}H_{26}Cl_2OS$: C, 73.77; H, 4.73. Found: C, 73.58; H, 4.97.

19c: MS (70 eV) *m/e* 554 (M^+, 8), 284 (100), 283 (90), 249 (81); NMR ($CDCl_3$) δ 2.00–2.90 (m, 8 H), 3.83 (d, 1 H, J = 11.0 Hz), 4.50 (d, 1 H, J = 11.0 Hz), 7.00–7.90 (m, 16 H). Anal. Calcd for $C_{34}H_{26}Cl_2OS$: C, 73.77; H, 4.73. Found: C, 73.64; H, 4.89.

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Registry No. **1a**, 67254-57-3; **1b**, 67314-93-6; **1c**, 70041-49-5; **2a**, 67254-58-4; **2b**, 67254-59-5; **2c**, 67254-60-8; **3a**, 71436-14-1; **3b**, 71436-15-2; **4a**, 71436-16-3; **4b**, 71436-17-4; **4c**, 71436-18-5; **5a**, 71436-19-6; **5b**, 71436-20-9; **6a**, 71436-21-0; **7a**, 71436-22-1; **7b**, 71436-23-2; **7c**, 71436-24-3; **8a**, 71436-25-4; **8b**, 71436-26-5; **9a**, 71436-27-6; **9b**, 71436-28-7; **9c**, 71436-29-8; **10a**, 71436-30-1; **10b**, 71436-31-2; **11a**, 71436-32-3; **11b**, 71436-33-4; **11c**, 71436-34-5; **12a**, 71436-35-6; **12b**, 71436-36-7; **13a**, 71436-37-8; **13b**, 71436-38-9; **13c**, 71436-39-0; **14a**, 71436-40-3; **14b**, 71436-41-4; **15a**, 71436-42-5; **15b**, 71436-43-6; **15c**, 71436-44-7; **16a**, 71436-45-8; **16b**, 71436-46-9; **17a**, 71436-47-0; **17b**, 71436-48-1; **18a**, 71436-49-2; **18b**, 71436-50-5; **18c**, 71436-51-6; **19a**, 71436-52-7; **19b**, 71436-53-8; **19c**, 71436-54-9; chalcone, 94-41-7; maleic anhydride, 108-31-6; styrene, 100-42-5; *n*-butyl vinyl ether, 111-34-2; norbornadiene, 121-46-0; citraconic anhydride, 616-02-4; norbornene, 498-66-8.

Supplementary Material Available: ^{13}C spectral data of compounds **12–15** (4 pages). Ordering information is given on any current masthead page.