Preparation of Some Polyfunctional Indenes and Indanones: The Reaction of Mercapto-Substituted Cyclopropenium Salts with Alcohols and Thiols

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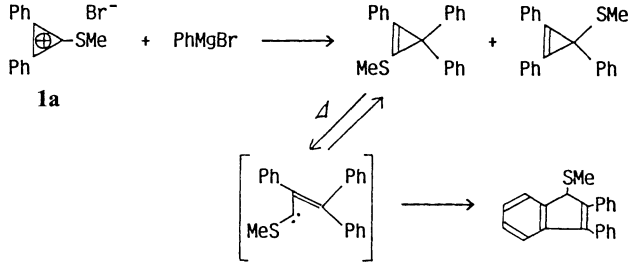
The reaction of 1-methylthio-, 1-(4-methylphenylthio)-, or 1-*t*-butylthio-2,3-diphenylcyclopropenium salts with alcohols, phenols, and thiols in the presence of triethylamine at around 80 °C gave 1*H*-indene-1-thiol derivatives in fair to moderate yields. In contrast, the same reactions at room temperature afforded 1-alkylthio- or arylthio-1-cyclopropene derivatives together with a small amount of the 3-isomer. Some 1-isomers were separated as pure crystals and produced the corresponding indenes in quantitative yields when heated. Kinetic studies of the ring-opening of cyclopropenes suggested a vinylcarbene intermediate based on the small effects of solvent polarities and phenoxyl substituents on the reaction rates. The reaction of diphenylcyclopropenone with thiol in the presence of trifluoroacetic acid yielded 1*H*-indene-1,3-dithiol detivatives via a 1,3-bis(alkylthio)-or (arylthio)-1-cyclopropene intermediate. On acidic hydrolysis of 3-alkoxyindenes and on heating of 3-allyloxy- and 3-(2-propynyloxy)indenes, polyfunctionally-substituted indanones were obtained in good yields.

In recent years, investigations of three membered carbocycles such as cyclopropane, cyclopropene, cyclopropenone, and cyclopropenium ion have been undertaken not only to satisfy physical interests but also to develop a versatile tool for organic syntheses.[1] In the series of our studies of the cyclopropenium salts bearing heteroatom substituents,[2] we have previously reported that the reaction of a mercapto-substituted cyclopropenium salt **1**, e.g. 1-methylthio-2,3-diphenylcyclopropenium bromide (**1a**) with acyclic[3] and cyclic 1,3-diketones[4] afforded pentadienols and 2*H*-pyranes, respectively. Furthermore, the reaction of **1a** with some Grignard reagents yielded a mixture of 1-methylthio- and 3-methylthiocyclopropenes, of which the former isomer lead to the ring opening products, indenes, via vinylcarbene intermediates (Scheme 1).[5]

Encouraged by these results, we undertook further studies of the reaction of **1** with other nucleophiles. We report here the reaction of **1** with alcohols, phenols, and thiols to produce polyfunctional indenes. Current interests in polysubstituted indenes have been focused on synthesis,[6] oxidation with ozone,[7] electrochemical reduction,[8] and application to medical chemistry.[9]

The salt **1a** has been prepared from methylation of diphenylcyclopropenethione,[3] whereas 1-(4-methylphenylthio)- and 1-*t*-butylthio-2,3-diphenylcyclopropenium tetrafluoroborates (**1b**, **c**) were obtained from the reaction of ethoxycyclopropenium tetrafluoroborate with thiols in good yields.

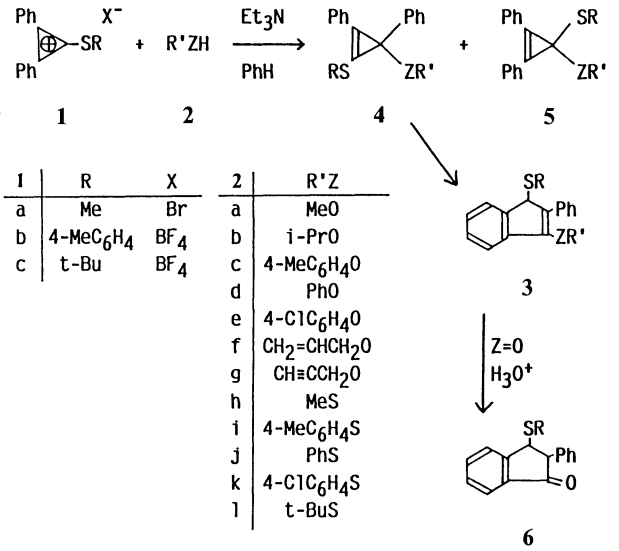


Scheme 1.

Treatment of a mixture of **1a**, methanol, and triethylamine (mole ratio, 1 : 1.1 : 3) in benzene at 80 °C afforded, after column chromatography over silica gel, 3-methoxy-1-methylthio-2-phenyl-1*H*-indene **3aa** in a 68% yield. The structure of the product was unequivocally established by ^{1}H and ^{13}C NMR and mass spectroscopic studies as well as by conversion to indanone **6a** upon standing in a hydrochloric acid–ethanol solution

Table 1. The Reaction of **1** with **2** in Benzene

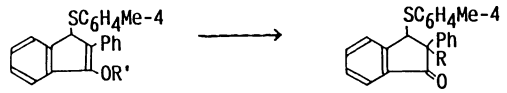
1	2	Reaction conditions		Product (yield/%)
		Temp/°C	Time/h	
1a	**2a**	80	1	**3aa** (68)
	2c	80	1	**3ac** (74)
	2d	80	1	**3ad** (49)
	2e	80	1	**3ae** (52)
	2h	80	0.5	**3ah** (71)
	2i	80	0.5	**3ai** (76)
	2j	80	0.5	**3aj** (63)
	2k	80	0.5	**3ak** (61)
	2l	80	0.5	**3al** (32)
1b	**2a**	25	1.5	**3ba** (75)
	2b	80	1	**3bb** (52)
	2c	80	1	**3bc** (82)
	2d	80	1	**3bd** (69)
	2e	80	1	**3be** (91)
	2f	80	1	**3bf** (19)
	2g	80	1	**3bg** (37)
1c	**2a**	25	2	**3ca** (65)
	2b	80	1	**3cb** (59)
	2c	80	1	**3cc** (84)
	2d	80	1	**3cd** (94)



1	R	X
a	Me	Br
b	4-MeC$_6$H$_4$	BF$_4$
c	t-Bu	BF$_4$

2	R'Z
a	MeO
b	i-PrO
c	4-MeC$_6$H$_4$O
d	PhO
e	4-ClC$_6$H$_4$O
f	CH$_2$=CHCH$_2$O
g	CH≡CCH$_2$O
h	MeS
i	4-MeC$_6$H$_4$S
j	PhS
k	4-ClC$_6$H$_4$S
l	t-BuS

Scheme 2.



3bf: R′=–CH$_2$CH=CH$_2$ **7a**: R=–CH$_2$CH=CH$_2$
3bg: R′=–CH$_2$C≡CH **7b**: R=–CH=C=CH$_2$

Scheme 3.

at room temperature for 2 d. Similar treatment of the salts **1a**—**c** with alcohols, phenols, or thiols (**2a**—**g**) afforded indenes **3** in fair to moderate yields (Table 1).

The conversion of indenes with 3-allyloxy- and 3-(2-propynyloxy)-substituents (**3bf** and **3bg**) to indanones **7a** and **7b** was accomplished by means of heating at benzene reflux temperature via a Claisen rearrangement (Scheme 3).

In order to detect the intermediate cyclopropenes, some controlled experiments were performed. Thus, the salt **1a** was treated with methanethiol **2h** in the presence of triethylamine at room temperature for 10 min. The crude product absorbed at around 1780 cm^{-1} in the IR spectrum indicating the presence of cyclopropenes. The ^{1}H NMR spectrum showed a mixture of the cyclopropenes **4ah** and **5ah** together with a small amount of the indene **3ah** (Table 2). The ratio was determined by the integration of methylthio groups of **3ah**, **4ah**, and **5ah**, whose signals appeared at δ=1.20 and 2.12, 1.85 and 2.47, and 2.03 respectively. Attempted isolation of pure **4ah** and **5ah** by cc or tlc was unsuccessful, since **4ah** was thermally unstable and produced the corresponding indene **3ah**, while **5ah** was converted to the cyclopropenone. On cooling to −20 °C, petroleum ether was added to the crude reaction mixture and some cyclopropenes **4** were recovered as crystals (Table 2). The structure of **4** was unambiguously determined from its ^{1}H and ^{13}C NMR, and mass spectra, and transformations to the corresponding indenes **3**. As summarized in Table 2, the crude reaction mixture also contained 3-mercaptocyclopropene **5**. Only **5ak** was isolated as an oil by a short column separation. Although attempts to isolate the other **5**'s failed, ^{1}H NMR and IR spectra as well as isolation of cyclopropenone from the cc elution indicated the presence of **5**.

Cyclopropenes prepared from the reactions of the salts **1b** and **1c** with alcohols were too unstable to isolate in a pure form even by separation on short cc or at lower temperatures.

The distribution of the products **4** and **5** suggested that the employed nucleophiles preferentially attacked the carbon atom unsubstituted by sulfur. This regioselectivity was attributed to the strong electron releasing properties of alkyl- or arylthio groups and steric repulsion between the phenyl substituent of **1** and the entering nucleophiles as have been observed for the reaction between **1** and Grignard reagents.[5]

Keeping a solution of **4** at around 20 to 80 °C resulted in the formation of the corresponding indene **3** in quantitative yields. Kinetic studies were performed in order to clarify the mechanism of the ring opening of **4** (Table 3). The rate was followed at suitable time intervals by analyzing the ^{1}H NMR spectra of the methylthio groups

Table 2. The Reaction of **1a** with **2** under Controlled Conditions

2	Mole ratio **1a**:**2**:amine	Time/min	Temp/°C	Products **4**:**5**[a]	(Isolation/%)[b]
2c	1:1:3 (Et$_3$N)	15	25	10:1	(**4ac**, 46)
2d	1:1:3 (Et$_3$N)	15	25	6:1	
	1:1:3 (Et$_3$N)	10	10	6:1	(**4ad**, 52)
	1:1:5 (Et$_3$N)	10	10	6:1	
	1:1:3 (Et$_2$NPr-*i*)	15	10	6:1	
2e	1:1:3 (Et$_3$N)	15	25	6:1	(**4ae**, 57)
2h		15	25	9:1	
2i		15	25	6:1	
2j		15	25	6:1	
2k		15	25	6:1	(**4ak**, 52; **5ak**, 2)
2l		15	25	7:2	

a) The ratio was determined by ^{1}H NMR spectroscopy using SMe signals. b) Isolation by low-temperature crystallization.

Table 3. Kinetic Studies of the Themal Ring-Opening of **4**

Reactant	Solvent (ε)	Temp/°C	$10^4\,k_1/s^{-1}$	
4ac	CCl_4 (2.2)	55.5	2.24±0.20	
4ad	CCl_4 (2.2)	55.5	1.81±0.11	
4ae	CCl_4 (2.2)	45.0	0.48±0.05	a)
		50.4	0.72±0.03	
		55.5	1.42±0.07	
		60.0	2.03±0.13	
	C_6D_6 (2.3)	50.4	0.52±0.05	
	1,2-$C_6H_4Cl_2$ (9.9)	50.4	1.02±0.09	
	PhCN (25.2)	45.0	0.84±0.04	b)
		50.4	1.51±0.11	
		55.5	2.14±0.14	
		60.0	4.81±0.17	
	$PhNO_2$ (34.6)	50.4	1.01±0.07	
4ak	CCl_4 (2.2)	45.4	0.64±0.05	c)
		50.4	0.99±0.09	
		55.5	1.98±0.18	
		60.0	2.68±0.19	

a) E_a=90.1±2.0 kJ mol^{-1}, $\Delta S^{\ddagger}$=−10.1±1.3 eu.
b) E_a=89.1±5.9 kJ mol^{-1}, $\Delta S^{\ddagger}$=−10.1±4.6 eu.
c) E_a=90.1±0.3 kJ mol^{-1}, $\Delta S^{\ddagger}$=−10.1±0.1 eu.

of **4** by using methyl phenyl sulfide or dimethyl sulfone as an internal standard. The disappearance of **4** showed good first-order rate constants (k_1). Small effects of phenoxy substituents (ρ=−0.51) and solvents polarities on the rate indicated the small ionization of the intermediates of ring opening.

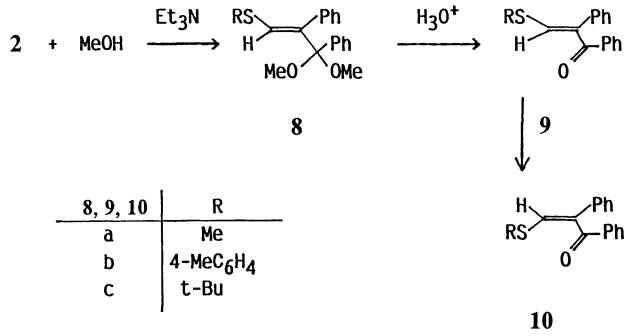
Tetraphenylcyclopropene has been reported to rearrange to indene with an activation energy of 167 kJ mol^{-1} (on heating at 240 °C),[10] while the activation energies of the rearrangement to **3** were only about 100 kJ mol^{-1}.

These results show that the ring opening of **4** proceeded via a vinylcarbene, stabilized by the adjacent mercapto group as shown in Scheme 1, followed by intramolecular hydrogen abstraction to produce indene **3**.

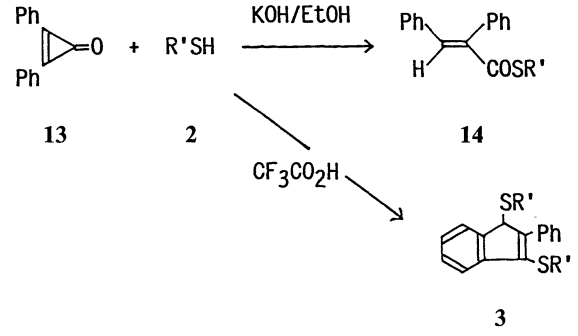
The following two reactions (Schemes 4 and 5) also provide support for the vinyl carbene intermediate for the ring opening of cyclopropenes. Treatment of **1** in methanol with triethylamine provided the methyl acetals **8a**, **b**, and **c** in 82, 86, and 85% yields respectively. Hydrolysis of **8** under acidic conditions afforded the vinyl ketones **9** in quantitative yields. Photoisomerization of **9c** in benzene yielded a 1 : 1 mixture of **9c** and **10**. The stereochemistry of **10** was assigned to *Z* on the basis of the ^{1}H NMR spectrum of the *t*-butylthio group at δ=1.39, because that of **9c** appeared at 1.33 (Scheme 4).

The cyclopropene **4ah** also reacted with refluxing methanol to give an unstable mixture of *E*- and *Z*-isomers of 3-methoxy-3-methylthio-1-propene **11** (Scheme 5). The structure was evident from the spectroscopic studies and conversion to the propenals **12** (Scheme 5). Although the two isomers could not be readily separated, high field ^{1}H NMR indicated that the *E*-isomer was the major product (10 : 3).

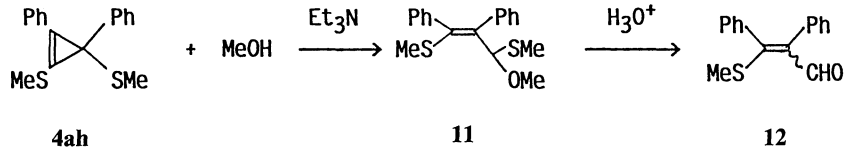
In our previous paper, we showed the reaction of cyclopropenone with thiol in the presence of potassium hydroxide in ethanol to yield thiolacrylates[11] (Scheme 6). Cyclopropenone is known to form a "salt"[12] with a Brönsted acid, and the salt is considered to be a hydroxy-substituted cyclopropenium.[11] It is reasonable to consider that the mercapto-substituted cyclopropenium ion would be generated in an acidic solution of cyclopropenone and thiol. This consideration was suggested by the following experiments. When a mixture of diphenylcyclopropenone **13**, methanethiol **2h**, and trifluoroacetic acid (mole ratio, 1 : 1 : 1) in benzene was heated at 60 °C, the indene **3ah** was obtained in a 15% yield along with **13** (70% recovery). The use of a mole rario of 1 : 3 : 3 resulted in better yields of **3** (Table 4). The ^{1}H NMR spectroscopic studies indicated that



Scheme 4.



Scheme 6.



Scheme 5.

Table 4. The Reaction of Cyclopropenone **13** with Thiol **2** in the Presence of Trifluoroacetic Acid

Thiol	Solvent	Temp/°C	Time/d	Product (Yield/%)
2h	PhH	60	5	**3ah** (57)
2i	PhH	80	1	**3bi** (72)
	EtOH	80	1	(61)
2j	PhH	80	1	**3jj** (72)
2k	PhH	80	1	**3kk** (86)
	EtOH	80	1	(55)
2l	PhH	80	3	None
	EtOH	80	3	**14** (52)

the reaction mixture with a ratio 1 : 3 : 3 in benzene after 1 h at room temperature contained a mixture of **3ah**, **4ah**, and **5ah** in a mole ratio of 1 : 4 : 1.4. Whereas the bulky thiol **2l** did not yield indene **3**, but the thioacrylate **14** (R′=*t*-Bu), similar treatment of thiols **2i**—**k** with **13** produced indenes **3** in moderate yields (Table 4). Thus, the indenes **3** were formed from 1,3-bis(alkylthio)- or 1,3-bis(arylthio)-1-cyclopropenes **4** even under acidic conditions.

Experimental

1) General. Melting points were uncorrected. The ^{1}H NMR spectra were recorded on a Hitachi R-24B (60 MHz) and the ^{13}C NMR spectra on a JEOL JNM FX-90Q (22.49 MHz) or EX-90 (22.50 MHz) spectrometer. The IR spectra were obtained on a JEOL JIR 100 spectrometer.

2) Preparation of 1-Mercapto-2,3-diphenylcyclopropenium Salts (1). 1-Methylthio-2,3-diphenylcyclopropenium bromide (**1a**) was prepared as previously described.[3] 1-(4-Methylphenylthio)-2,3-diphenylcyclopropenium tetrafluoroborate (**1b**) was prepared as follows. A solution of triethyloxonium tetrafluoroborate (1.9 g, 10 mmol) and diphenylcyclopropenone (2.06 g, 10 mmol) in dichloromethane (10 cm^3) was stirred at room temperature for 2 h. To the mixture was added 4-thiocresol (1.24 g, 10 mmol) in one portion. 1 h later the precipitates were collected, washed with dry benzene, and dried in vacuo. **1b:** 2.8 g (85%); mp, 204—206 °C; IR (KBr) 1820 cm^{-1}; ^{1}H NMR ($CDCl_3$+CF_3CO_2H, 5 : 1) δ=2.52 (s, 3H, Me) and 7.3—8.2 (m, 14H, arom). The salt **1c** was prepared similarly. The only different point was that benzene was added to the reaction mixture to precipitate the salt. **1c:** 3.12 g (80%); mp 130—133 °C; IR (KBr) 1820 cm^{-1}; ($CDCl_3$+CF_3CO_2H, 5 : 1) δ=1.82 (s, 9H, *t*-Bu) and 7.6—8.4 (m, 10H, 2Ph).

3) The Reaction of 1 with Alcohols, Phenols, and Thiols (2). A mixture of **1** (2.0 mmol), **2** (2.2 mmol), and triethylamine (6.0 mmol) in dry benzene (15 cm^3) was stirred well at an appropriate temperature. The reactions with thiols were carried out in sealed tubes. The resulting solution was washed with aqueous sodium hydroxide (0.5% solution), dried over anhydrous sodium carbonate, and condensed in vacuo. The reactions at 80 °C yielded pure **3** on recrystallization from methanol unless otherwise stated (Table 1). The controlled reactions for shorter times at lower temperatures afforded a mixture of cyclopropenes (**4** and **5**). To the crude product was added petroleum ether and the mixture was cooled to −20 °C to afford crystalline **4**. In only one case was **5ak** provided after a short cc over silica gel (Table 2). The physical properties of **3**, **4**, and **5** were as follows.

3aa: Mp 82—84 °C; IR (KBr) 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.25 (s, 3H, MeS), 3.74 (s, 3H, MeO), 4.58 (s, 1H, CH), and 6.8—8.0 (m, 9H, arom); MS (*m*/*z*), 268 (M$^+$). Found: C, 75.87; H, 5.99%. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 5.96%.

3ac: Mp 97—100 °C; IR (KBr) 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.48 (s, 3H, MeS), 2.28 (s, 3H, Me), 4.86 (s, 1H, CH), and 6.6—8.0 (m, 13H, arom); ^{13}C NMR ($CDCl_3$) δ=9.2 (q, MeS), 20.6 (q, Me), 47.8 (d, CH), 116.1 (d), 119.6 (d), 124.2 (d), 126.4 (d), 127.2 (d), 127.6 (d), 128.1 (d), 128.2 (d), 130.1 (d), 132.1 (s), 132.2 (s), 138.7 (s), 143.1 (s), and 149.3 (s); MS (*m*/*z*), 344 (M$^+$). Found C, 80.25; H, 5.78%. Calcd for $C_{23}H_{20}OS$: C, 80.19; H, 5.85%.

3ad: Mp 79—80 °C IR (KBr) 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.51 (s, 3H, MeS), 4.87 (s, 1H, CH), and 6.5—7.9 (m, 14H, arom); ^{13}C NMR ($CDCl_3$) δ=9.3 (q, MeS), 47.8 (d, CH), 116.7 (d), 119.6 (d), 122.7 (d), 124.3 (d), 126.5 (d), 127.3 (d), 127.4 (d), 128.0 (d), 128.2 (d), 128.3 (d), 130.0 (s), 132.2 (s), 138.6 (s), 143.1 (s), 149.0 (s), and 156.1 (s); MS (*m*/*z*), 330 (M$^+$). Found C, 79.90; H, 5.62%. Calcd for $C_{22}H_{18}OS$: C, 79.96; H, 5.49%.

3ae: Mp 142—145 °C; IR (KBr) 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.40 (s, 3H, MeS), 4.87 (s, 1H, CH), and 6.7—7.9 (m, 13H, arom); MS (*m*/*z*), 364 (M$^+$). Found C, 72.54; H, 4.57%. Calcd for $C_{22}H_{17}ClOS$: C, 72.41; H, 4.69%.

3ah: Mp 94—96 °C; ^{1}H NMR ($CDCl_3$) δ=1.22 (s, 3H, Me), 2.12 (s, 3H, Me), 4.71 (s, 1H, CH), and 6.8—7.9 (m, 9H, arom); ^{13}C NMR ($CDCl_3$) δ=9.0 (q, Me), 17.1 (q, Me), 52.4 (d, CH), 120.2 (d), 123.9 (d), 126.2 (d), 127.6 (d), 127.7 (d), 127.9 (d), 129.3 (d), 133.7 (s), 134.4 (s), 142.9 (s), 144.0 (s), and 147.0 (s); MS (*m*/*z*), 284 (M$^+$). Found C, 71.68; H, 5.73%. Calcd for $C_{17}H_{16}S_2$: C, 71.78; H, 5.66%.

3ai: Mp 124—126 °C (hexane); ^{1}H NMR ($CDCl_3$) δ=1.38 (s, 3H, MeS), 2.20 (s, 3H, Me), 4.88 (s, 1H, CH), and 6.8—7.9 (m, 13H, arom); MS (*m*/*z*), 360 (M$^+$). Found C, 76.73; H, 5.52%. Calcd for $C_{23}H_{20}S_2$: C, 76.62; H, 5.59%.

3aj: Mp 128—129 °C; ^{1}H NMR ($CDCl_3$) δ=1.35 (s, 3H, MeS), 4.90 (s, 1H, CH), and 6.8—7.9 (m, 14H, arom); MS (*m*/*z*), 346 (M$^+$). Found C, 76.36; H, 5.29%. Calcd for $C_{22}H_{18}S_2$: C, 76.26; H, 5.24%.

3ak: Mp 119—121 °C; ^{1}H NMR ($CDCl_3$) δ=1.41 (s, 3H, MeS), 4.95 (s, 1H, CH), and 7.1—7.7 (m, 13H, arom); MS (*m*/*z*), 380 (M$^+$). Found C, 69.43; H, 4.54%. Calcd for $C_{22}H_{17}ClS_2$: C, 69.36; H, 4.49%.

3al: Mp 87—90 °C; ^{1}H NMR ($CDCl_3$) δ=1.08 (s, 9H, Bu-*t*), 1.23 (s, 3H, MeS), 4.76 (s, 1H, CH), and 7.0—7.6 (m, 9H, arom); MS (*m*/*z*), 326 (M$^+$). Found C, 73.68; H, 6.68%. Calcd for $C_{20}H_{22}S_2$: C, 73.57; H, 6.79%.

3ba: Mp 79—81 °C; IR (KBr) 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.08 (s, 3H, Me), 3.58 (s, 3H, MeO), 4.87 (s, 1H, CH), and 6.6—7.9 (m, 13H, arom); MS (*m*/*z*), 344 (M$^+$). Found C, 80.04; H, 5.93%. Calcd for $C_{23}H_{20}OS$: C, 80.19; H, 5.85%.

3bb: Mp 76 °C; IR (KBr) 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.14 (d, *J*=7 Hz, 6H, 2Me), 2.15 (s, 3H, Me), 4.35 (sept, 1H, CH), 4.96 (s, 1H, CH), and 6.5—8.1 (m, 13H, arom); MS (*m*/*z*), 372 (M$^+$). Found C, 80.74; H, 6.43%. Calcd for $C_{25}H_{24}OS$: C, 80.60; H, 6.49%.

3bc: Mp 198—199 °C; IR (KBr) 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.30 (S, 6H, 2Me), 4.99 (s, 1H, CH), and 6.2—7.8 (m, 17H, arom); ^{13}C NMR ($CDCl_3$) δ=20.6 (q, Me), 21.2 (q, Me), 51.5 (d, CH), 116.1 (d), 119.7 (d), 124.6 (d), 126.1 (d),

126.3 (d), 127.1 (d), 128.0 (d), 128.3 (d), 128.4 (d), 129.0 (d), 129.9 (d), 131.8 (s), 132.6 (s), 136.0 (s), 138.5 (d), 138.7 (s), 143.8 (s), 149.5 (s), and 154.1 (s); MS (*m/z*), 420 (M^+). Found C, 82.90; H, 5.68%. Calcd for $C_{29}H_{24}OS$: C, 82.82; H, 5.75%.

3bd: Mp 131—134 °C; IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.26 (s, 3H, Me), 5.04 (s, 1H, CH), and 6.3—7.9 (m, 18H, arom); ^{13}C NMR ($CDCl_3$) δ=21.2 (q, Me), 51.4 (d, CH), 116.3 (d), 119.6 (d), 122.4 (d), 124.7 (d), 126.1 (d), 127.2 (d), 128.1 (d), 128.3 (s), 128.4 (d), 129.0 (d), 130.2 (s), 130.9 (s), 132.5 (d), 136.0 (d), 138.4 (s), 138.8 (s), 143.7 (s), 149.2 (s), and 156.2 (s); MS (*m/z*), 406 (M^+). Found C, 82.59; H, 5.52%. Calcd for $C_{28}H_{22}OS$: C, 82.72; H, 5.45%.

3be: Mp 192—194 °C; IR (KBr) 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.25 (s, 3H, Me), 5.00 (s, 1H, CH), and 6.3—7.9 (m, 17H, arom); MS (*m/z*), 440 (M^+). Found C, 76.21; H, 4.75%. Calcd for $C_{28}H_{21}ClOS$: C, 76.26; H, 4.79%.

3bf: Mp 55—56 °C (petroleum ether); IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.18 (s, 3H, Me), 4.15—4.40 (m, 2H, CH_2), 4.88 (s, 1H, CH), 5.50 (m, 2H, CH_2O), and 6.4—7.8 (m, 13H, arom); MS (*m/z*), 370 (M^+). Found: C, 81.22; H, 5.91%. Calcd for $C_{25}H_{22}OS$: C, 81.04; H, 5.98%.

3bg: Mp 55—56 °C (petroleum ether); IR (KBr) 2140 and 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.15 (s, 3H, Me), 2.40 (t, *J*=3 Hz, 1H, CH), 4.39 (d, *J*=3 Hz, 2H, CH_2), 4.89 (s, 1H, CH), and 6.9—7.8 (m, 13H, arom); ^{13}C NMR ($CDCl_3$) δ=21.2 (q, Me), 51.9 (d), 59.0 (t), 78.8 (s, $\underline{C}CH$), 118.8 (d), 124.1 (s), 124.4 (d), 126.3 (d), 127.1 (d), 127.4 (d), 128.2 (d), 128.7 (d), 128.9 (d), 129.8 (s), 132.2 (s), 134.9 (d), 138.3 (s), 139.3 (s), 143.6 (s), and 153.8 (s); MS (*m/z*), 368 (M^+). Found C, 81.42; H, 5.54%. Calcd for $C_{25}H_{19}OS$: C, 81.48; H, 5.47%.

3ca: Mp 116 °C; IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.01 (s, 9H, Bu-*t*), 3.72 (s, 3H, MeO), 4.64 (s, 1H, CH), and 7.0—8.1 (m, 9H, arom); MS (*m/z*), 310 (M^+). Found C, 77.43; H, 7.03%. Calcd for $C_{20}H_{22}OS$: C, 77.37; H, 7.14%.

3cb: Mp 76 °C; IR (KBr) 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.14 (d, *J*=7 Hz, 2Me), 2.15 (s, 3H, Me), 4.35 (sept, 1H, CH), 4.96 (s, 1H, CH), and 6.5—8.1 (m, 13H, arom); MS (*m/z*), 338 (M^+). Found C, 78.14; H, 7.79%. Calcd for $C_{22}H_{26}OS$: C, 78.06; H, 7.74%.

3cc: Mp 129—130 °C IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.10 (s, 9H, Bu-*t*), 4.89 (s, 1H, CH), and 6.2—7.8 (m, 17H, arom); ^{13}C NMR ($CDCl_3$) δ=20.6 (q, Me), 32.3 (q, 3Me), 45.7 (s, $\underline{C}Me_3$), 48.8 (d, CH), 116.2 (d), 119.9 (d), 124.8 (d), 126.1 (d), 127.0 (d), 128.0 (d), 128.7 (d), 129.9 (s), 130.0 (d), 131.9 (s), 133.0 (s), 137.8 (s), 145.5 (s), 148.5 (s), and 154.3 (s); MS (*m/z*), 386 (M^+). Found C, 80.67; H, 6.79%. Calcd for $C_{26}H_{26}OS$: C, 80.78; H, 6.77%.

3cd: Oil; IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.12 (s, 9H, Bu-*t*), 4.93 (s, 1H, CH), and 6.7—7.8 (m, 13H, arom); MS (*m/z*), 372 (M^+). Found C, 80.69; H, 6.53%. Calcd for $C_{25}H_{24}OS$: C, 80.60;, H, 6.49%.

4ac: Mp 99—100 °C; IR (KBr) 1780 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.19 (s, 3H, Me), 2.56 (s, 3H, MeS), and 6.6—7.9 (m, 14H, arom); ^{13}C NMR (C_6D_6) δ=16.7 (q, MeS), 20.5 (q, Me), 69.5 (s, C_3), 118.3 (d), 118.7 (s), 119.3 (s), 126.9 (d), 128.5 (d), 128.7 (d), 128.9 (d), 130.0 (d), 130.5 (s), 142.3 (s), and 155.7 (s); MS (*m/z*), 343 (M^+−1). Found C, 80.09; H, 5.77%. Calcd for $C_{23}H_{20}OS$: C, 80.19; H, 5.85%.

4ad: Mp 107—108 °C; IR (KBr) 1790 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.59 (s, 3H, Me) and 6.5—7.9 (m, 15H, arom); ^{13}C NMR (C_6D_6) δ=16.7 (q, MeS), 69.2 (s, C_3), 118.0 (d), 118.4 (s), 119.3 (s), 121.4 (d), 126.6 (d), 126.9 (d), 128.4 (d), 128.7 (d), 128.9 (d), 129.5 (d), 129.9 (s), 142.0 (s), and 158.0 (s); MS (*m/z*), 330 (M^+). Found C, 80.06; H, 5.47%. Calcd for $C_{22}H_{18}OS$: C, 79.96; H, 5.49%.

4ae: Mp 122—124 °C; IR (KBr) 1785 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.65 (s, 3H, Me) and 6.7—7.8 (m, 14H, arom); ^{13}C NMR (C_6D_6) δ=16.8 (sm Me), 69.7 (s, C_3), 118.2 (s), 119.4 (d), 121.7 (s), 126.4 (d), 126.5 (d), 127.2 (d), 128.2 (d), 128.8 (d), 129.0 (d), 129.5 (d), 129.9 (s), 141.5 (s), and 156.6 (s); MS (*m/z*), 364 (M^+). Found C, 72.24; H, 4.55%. Calcd for $C_{22}H_{17}ClOS$: C, 72.41; H, 4.69%.

4ak: Mp 100—102 °C; IR (KBr) 1780 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.18 (s, 3H, Me) and 6.8—7.8 (m, 14H, arom); ^{13}C NMR (C_6D_6) δ=15.6 (q, Me), 30.1 (s, C_3), 122.3 (d), 127.4 (s), 127.6 (d), 128.3 (d), 128.7 (d), 129.8 (d), 130.0 (d), 132.9 (s), 134.8 (d), 135.5 (s), and 137.8 (s); MS (*m/z*), 380 (M^+). Found C, 69.31; H, 4.29%. Calcd for $C_{22}H_{17}ClS_2$: C, 69.36; H, 4.49%.

5ak: Oil; IR (KBr) 1820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.25 (s, 3H, Me) and 6.3—8.0 (m, 14H, arom); ^{13}C NMR (C_6D_6) δ=1.3 (q, Me), 17.2 (s, C_3), 127.4 (s), 128.3 (d), 128.5 (d), 128.7 (d), 129.8 (d), 131.4 (s), 136.9 (s), 139.3 (s), and 147.3 (d); MS (*m/z*), 333 (M^+−1).

Hydrolysis of **3aa** or **3ba** (0.5 mmol) in a mixture of ethanol (10 cm^3) and 3 mol dm^{-3} aqueous HCl (15 cm^3) for 2 d at room temperature yielded 3-methylthio- or 3-(4-methylphenylthio)-2-phenyl-1-indanone [**6a**(R=Me) or **6b**(R=4-MeC_6H_4)] in 92 or 94% yields.

6a: Mp 76—77 °C (MeOH); IR (KBr) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.93 (s, 3H, Me), 3.79 (d, *J*=4 Hz, 1H, C_2H), 4.35 (d, *J*=4 Hz, 1H, and C_3H), and 6.9—7.9 (m, 9H, arom); MS (*m/z*), 254 (M^+). Found C, 75.49; H, 5.43%. Calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.54%.

6b: Mp 102—104 °C (MeOH); IR (KBr) 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.19 (s, 3H, Me), 3.70 (d, *J*=4 Hz, C_2H), 4.60 (d, *J*=4 Hz, C_1H), and 6.5—7.9 (m, 13H, arom); MS (*m/z*), 330 (M^+). Found C, 79.91; H, 5.58%. Calcd for $C_{22}H_{18}OS$: C, 79.96; H, 5.49%.

Heating **3bf** and **3bg** in refluxing benzene for 2 d provided **7a** and **7b** in 95 and 92% yields, respectively, on crystallization from petroleum ether.

7a: Mp 119—122 °C; IR (KBr) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.20 (s, 3H, Me), 2.48—3.45 (m, 2H, CH_2), 4.7—5.2 (m, 2H, CH_2), 4.94 (s, 1H, C_1H), 5.2—6.1 (m, 1H, CH), and 6.4—7.8 (m, 13H, arom); MS (*m/z*), 370 (M^+). Found C, 80.89; H, 5.91%. Calcd for $C_{25}H_{22}OS$: C, 81.04; H, 5.98%.

7b: Mp 119—121 °C; IR (KBr) 1950 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.32 (s, 3H, Me), 4.81 (d, *J*=6 Hz, 2H, CH_2), 5.21 (s, 1H, C_1H), 5.70 (t, *J*=6 Hz, CH), and 6.5—8.0 (m, 13H, arom); ^{13}C NMR ($CDCl_3$) δ=21.0 (q, Me), 56.8 (d, C_3), 62.5 (s, C_2) 79.6 (t), 94.1 (d), 124.3 (s), 126.6 (s), 127.6 (d), 127.8 (d), 128.8 (d), 129.0 (d), 129.5 (d), 131.9 (d), 132.2 (d), 134.7 (s), 135.4 (d), 137.3 (s), 139.7 (s), 154.2 (s), 202.7 (s, CO), and 207.0 (s, =C=); MS (*m/z*), 368(M^+). Found C, 81.43; H, 5.55%. Calcd for $C_{25}H_{20}OS$: C, 81.48; H, 5.47%.

4) Kinetic Investigation of the Thermolysis of 4. A solution of **4** and methyl phenyl sulfide (or dimethyl sulfone) in an appropriate solvent was sealed in an NMR tube and was kept standing in a thermostated bath (±0.1 °C); the rate was followed at suitable time intervals by analyzing the ^1H NMR spectra of the methylthio groups of **3**, **4**, and the internal standard. The results are collected in Table 3.

5) Methanolysis of 1. A solution of **1** (2 mmol) and triethylamine (6 mmol) in methanol (15 cm^3) was refluxed for

1 h. The solution was quenched with aqueous NaOH (0.1%) and the organic product was extracted with benzene. The usual workup, followed by recrystallization from chloroform–petroleum ether, yielded the 2-propenalacetals **8**.

8a: 82%; mp 103—105 °C; IR (KBr) 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.29 (s, 3H, MeS), 3.14 (s, 6H, 2MeO), and 6.7—7.8 (m, 11H, arom and =CH); ^{13}C NMR ($CDCl_3$) δ=17.4 (q, MeS), 49.1 (s, MeO), 103.0 (s), 126.9 (d), 127.5 (d), 129.3 (d), 131.0 (d), 136.5 (s), 137.5 (s), and 140.2 (s); MS (*m/z*), 300 (M^+). Found C, 71.83; H, 6.71%. Calcd for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.71%.

8b: 86%; mp 90—93 °C: IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.32 (s, 3H, Me), 3.20 (s, 6H, 2MeO), and 6.7—7.5 (m, 14H, arom and =CH); ^{13}C NMR ($CDCl_3$) δ=21.0 (q, Me), 49.2 (q, MeO), 102.9 (s), 127.3 (d), 127.4 (d), 127.6 (d), 128.1 (d), 128.9 (d), 129.3 (d), 129.5 (d), 129.8 (d), 130.1 (d), 132.6 (s), 137.1 (s), 138.0 (s), and 139.9 (s); MS (*m/z*), 376 (M^+). Found C, 76.59; H, 6.24%. Calcd for $C_{24}H_{24}O_2S$: C, 76.56; H, 6.42%.

8c: 85%; mp 74—77 °C IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40 (s, 9H, Bu-*t*), 3.19 (s, 6H, 2MeO), and 7.0—7.6 (m, 11H, arom and =CH); ^{13}C NMR ($CDCl_3$) δ=31.1 (q, 3Me), 43.6 (s, $\underline{C}Me_3$), 49.2 (s, MeO), 103.0 (s), 125.5 (d), 126.9 (d), 127.4 (d), 128.2 (d), 129.3 (d), 131.4 (d), 136.7 (s), 137.7 (s), and 140.3 (s); MS (*m/z*), 342 (M^+). Found C, 73.75; H, 7.87%. Calcd for $C_{21}H_{26}O_2S$: C, 73.64; H, 7.65%.

Hydrolysis of **8** (2 mmol) in a mixture of methanol (15 cm^3) and aqueous HCl (3 mol dm^{-3}, 10 cm^3) at room temperature for 1 d afforded phenyl vinyl ketones **9** in a quantitative yield from chloroform–petroleum ether.

9a: Mp 59—61 °C; IR (KBr) 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.29 (s, 3H, Me) and 6.8—7.9 (m, 11H, arom and =CH); ^{13}C NMR ($CDCl_3$) δ=18.0 (q, Me), 127.7 (d), 128.0 (d), 128.2 (d), 129.2 (d), 131.4 (d), 135.9 (s), 136.4 (s), 138.6 (s), 148.9 (d), and 193.2 (s, C=O); MS (*m/z*), 254 (M^+). Found C, 75.71; H, 5.42%. Calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.54%.

9b: Mp 59—60 °C; IR (KBr) 1645 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.25 (s, 3H, Me) and 6.5—7.9 (m, 15H, arom and =CH); ^{13}C NMR ($CDCl_3$) δ=21.0 (q, Me), 128.0 (d), 128.1 (d), 128.3 (d), 129.3 (d), 129.5 (d), 130.1 (d), 130.6 (d), 130.8 (d), 131.6 (d), 135.8 (d), 136.8 (s), 138.3 (s), 138.4 (s), 146.5 (d), and 193.4 (s, C=O); MS (*m/z*), 330 (M^+). Found C, 79.88; H, 5.44%. Calcd for $C_{22}H_{18}OS$: C, 79.96; H, 5.49%.

9c: Mp 83—86 °C; IR (KBr) 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.33 (s, 9H, 3Me) and 7.2—7.8 (m, 11H, arom and =CH); ^{13}C NMR ($CDCl_3$) δ=30.9 (q, 3Me), 45.4 (s, $\underline{C}Me_3$), 127.7 (d), 128.0 (d), 128.2 (d), 129.3 (d), 129.4 (d), 131.4 (d), 136.0 (s), 138.9 (s), 144.4 (d), and 193.6 (s, C=O); MS (*m/z*), 296 (M^+). Found C, 77.18; H, 6.64%. Calcd for $C_{19}H_{20}OS$: C, 76.98; H, 6.80%.

The stereochemistry of **9c** was studied under irradiation by a high pressure mercury lamp. The initial signal at δ=3.19 decreased and a new signal at δ=3.44 appeared in equal strength.

6) Methanolysis of 4ah. A crude product mixture of **4ah** and **5ah** (9 : 1, 2 mmol) (obtained from the predescribed workup) was heated at reflux temperature in methanol (10 cm^3) containing 0.5% NaOH for 1 d. The usual workup gave an acid-sensitive oil, whose ^1H NMR spectrum showed major peaks at δ=1.60, 1.79, 1.90, 2.12, 2.18 (MeS's), 3.16, 3.20, and 3.47 (MeO's). An acid hydrolysis with a solution of aqueous HCl (3 mol dm^{-3}, 5 cm^3) in ethanol (5 cm^3) at room temperature for 1 d yielded a mixture of aldehyde **12** in a 53% yield after a short column chromatography over silica gel. The separation of *E*- and *Z*- isomers was unsuccessful.

12: Oil, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.74 and 1.92 (s, 1 : 0.3, 3H, MeS), 6.8—7.7 (m, 10H, 2Ph), 9.19 and 10.35 (s, 1 : 0.3, 1H, CHO); MS (*m/z*), 254 (M^+). Found C, 75.47; H, 5.61%. Calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.54%.

7) The Reaction of Diphenylcyclopropenone 13 with Thiol 2 in the Presence of Trifluoroacetic Acid. General Procedure. A mixture of **2**, **13**, and trifluoroacetic acid (3, 1, and 3 mmol, respectively) in benzene or ethanol (5 cm^3) was heated in a sealed tube for an appropriate time. The usual workup in the manner described above yielded indene **3** or thiolacrylate **14** (R′=Bu-*t*) by recrystallization from methanol. The results are collected in Table 4.

3bi: Mp 177—178 °C; ^1H NMR δ=2.22 (s, 3H Me), 2.25 (s, 3H, Me), 5.07 (s, 1H, CH), and 6.5—7.8 (m, 17H, Ar); MS (*m/z*), 436 (M^+). Found: C, 79.62; H, 5.65%. Calcd for $C_{29}H_{24}S_2$: C, 79.76; H, 5.55%.

3jj: Mp 127—128 °C; IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.13 (s, 1H, CH) and 6.5—7.8 (m, 19H, arom); MS (*m/z*), 408 (M^+). Found C, 79.57; H, 4.84%. Calcd for $C_{27}H_{20}S_2$: C, 79.37; H, 4.93%.

3kk: Mp 186—187 °C; IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.12 (s, 1H, CH) and 6.5—7.9 (m, 17H, arom); MS (*m/z*), 476 (M^+). Found C, 67.79; H, 3.58%. Calcd for $C_{27}H_{18}Cl_2S_2$: C, 67.92; H, 3.79%.

14 (R′=Bu-*t*): Mp 109—111 °C (lit,[11] 109—111 °C).

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