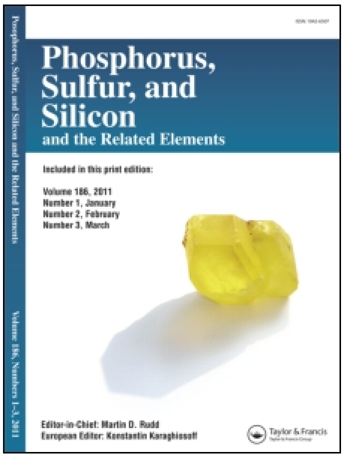

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REACTIONS OF CYCLIC β-KETO SULFONIUM YLIDES[1]

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The reaction of representative cyclic carbonyl-stabilized ylides with a variety of electrophiles has been examined. The ylides have been shown to react at the ylide carbanion with dimethyl acetylenedicarboxylate, tetracyanoethylene, and acetic anhydride to produce new carbonyl-stabilized ylides, and at the carbonyl oxygen with 2,3-diphenyl-2-cyclopropen-1-one and 2,3-diphenyl-2-cyclopropene-1-thione to produce pyranone derivatives.

INTRODUCTION

Sulfonium ylides are very useful reagents in synthetic organic chemistry.[2] These ylides have been used as alkylidene transfer reagents to the double bond of carbonyl or olefin derivatives to afford oxiranes,[3] aziridines,[4] or cyclopropanes,[5] respectively. Ring expansion of sulfonium ylides is also a useful procedure to prepare medium-ring compounds,[6] or furan derivatives.[7]

Until now, the majority of reactions of sulfonium ylides reported have been of acyclic ylides.[2] Little attention has been devoted to the reactions of electrophiles with cyclic sulfonium ylides since such ylides are usually very labile compared with the open-chain analogues.[8]

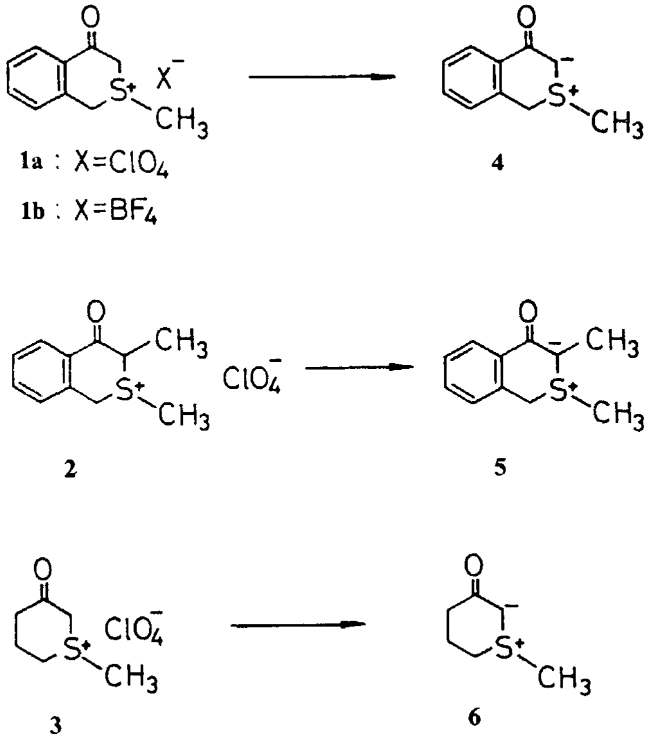
We describe here the details of our study on cyclic β-keto sulfonium ylides.

RESULTS AND DISCUSSION

Sulfonium salts **1**, **2**, and **3** were prepared from the corresponding cyclic sulfides by the method of Caserio[9] (Scheme 1).

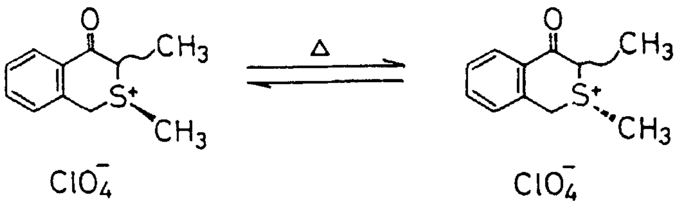
The reactions of ylide **4**, carried out in methanol or dichloromethane solution by adding an electrophile, are summarized in Table I.

New stable ylides **7**, **8**, and **9** were formed by treatment of the ylide **4** with dimethyl acetylenedicarboxylate, tetracyanoethylene, and acetic anhydride.[10] The structures of these new ylides were established by comparison of their ^{1}H NMR spectra to the starting ylide **4**; the benzylic protons of **7**, **8**, and **9** appear in 3.8–5.0 ppm region as AB quartets. In these reactions, proton transfer of the initial adduct takes precedence over cyclopropane formation.[5g, 10c] The reactions of these ylides with 2,3-diphenyl-2-cyclopropen-1-one (**12**) and its thione analogue **13** gave pyranone derivatives.[11] The formation of these pyranone derivatives parallels that of similar reactions involving dimethylsulfonium phenacylide.[11]



SCHEME 1

Sulfonium salt **2** was prepared from 3-methylisothiochroman-4-one[12] and iodomethane as a mixture of diastereomers; samples of trans/cis ratio of 1 : 12 and 10 : 1.8 ratio were obtained by recrystallization from acetonitrile–ethanol. No appreciable trans/cis isomerization was observed by ^{1}H NMR analysis when a CD_3CN solution of the sulfonium salt **2** was allowed to stand at room temperature for 8 days; rapid pyramidal inversion, leading to a trans/cis mixture in the ratio of 1.2 : 1 (Eq. (1)), was observed at 110°C.

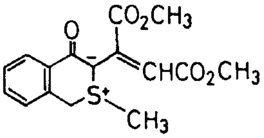
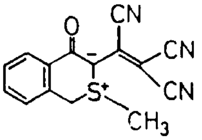
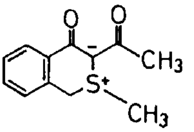
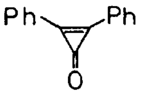
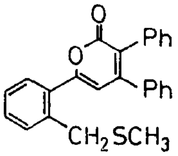
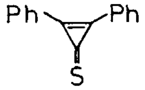
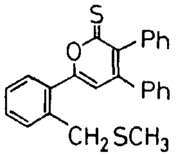


(1)

Ylide **5**, prepared in 79% yield by reaction of **2** with sodium methoxide in methanol at 0°C (Figure 1), is stable at room temperature for several months; some decomposition was observed by ^{1}H NMR analysis when stored for 6 days in chloroform. It is interesting to point out that exposure of **5** to CH_3OD at room temperature for 1 h caused complete disappearance of the methylene protons[9] (Eq.

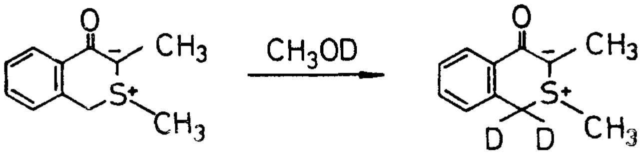
TABLE I

Reactions of ylides **4**.

Electrophile	Product		Reaction condn		Solvent	Yield[a] (%)
			Time (h)	Temp. (°C)		
$CH_3O_2CC{\equiv}CCO_2CH_3$		**(7)**	14	0	CH_3OH	72
$(NC)_2C{=}C(CN)_2$		**(8)**	0.5	R.T.	CH_3OH	71
$(CH_3CO)_2O$		**(9)**	10	R.T.	CH_2Cl_2	14
		**(10)**	18	R.T.	CH_3OH	50
		**(11)**	24	0	CH_3OH	53

[a] No effort to maximize the yield was made.

(2)). Reaction of the ylide **5** with **12** and **13** yielded the corresponding pyranone derivatives, **14** (66%), and **15** (75%), respectively (Eq. (3)).



5 **16** (2)

Attempts to isolate ylide **6** in pure form were unsuccessful owing to its lability at room temperature. Treatment of the ylide **6** generated *in situ* from sulfonium salt **3** with **12**, or **13** gave similar pyranone derivatives, **17** (57%), or **18** (79%), respectively (Eq. (4)).

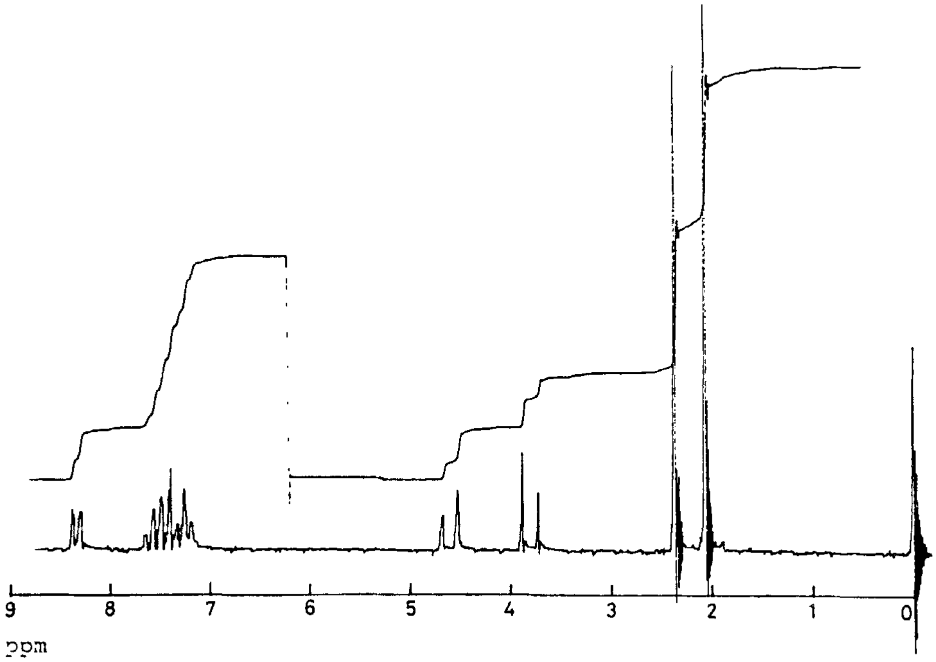
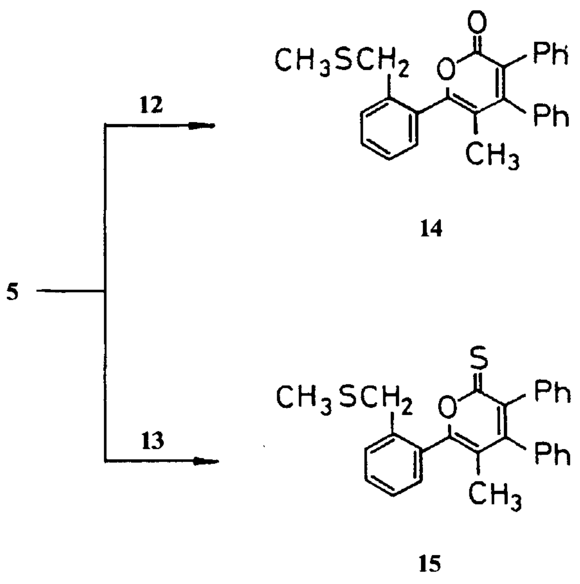
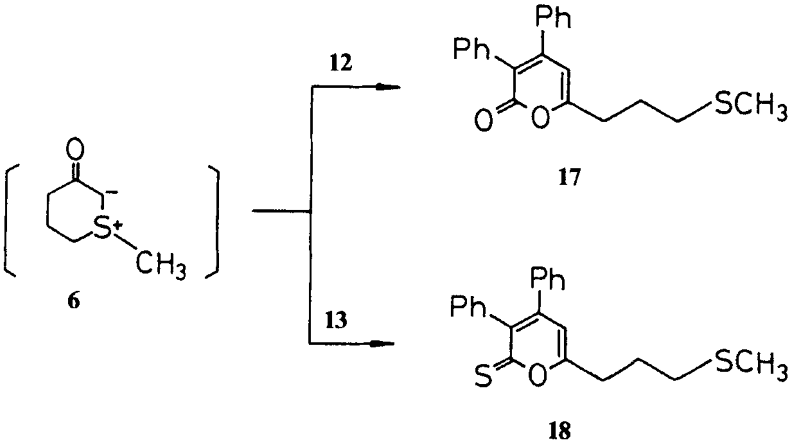


FIGURE 1 ^1H NMR (100-MHz) spectra of ylide **5** in $CDCl_3$.

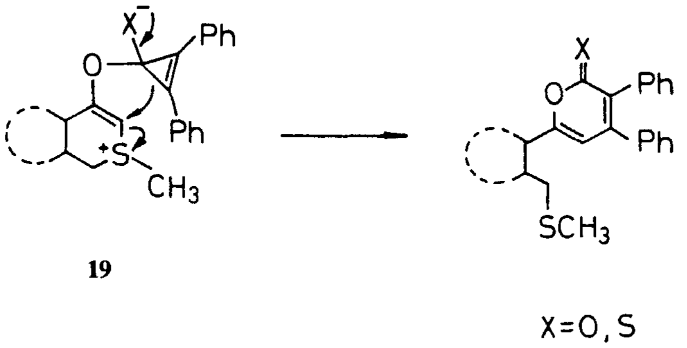
These reactions of cyclic ylides **4**, **5**, and **6** with **12** or **13** are believed to proceed stepwise via addition of the ylide to the carbonyl carbon to give the intermediate **19** followed by ring expansion of the cyclopropenone with displacement of the methylthiomethyl moiety (Eq. (5)).



(3)

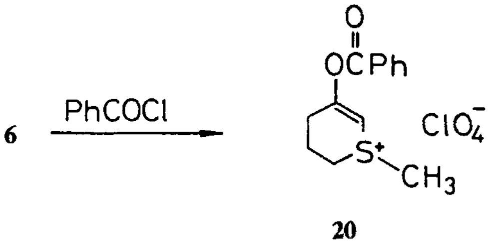


(4)



(5)

In contrast, 3-benzoyloxy-1-methyl-thioniacyclohex-3-ene perchlorate (**20**) was observed as the main product from reaction of the ylide **6** with benzoyl chloride in dry acetone (Eq. (6)). In the ^1H NMR spectrum, the characteristic olefinic proton appeared at 6.50 ppm. In addition, IR analysis showed C—O—C stretching at 1236 cm^{-1}, indicating the presence of an ester group. Several attempts to prepare stable ylides from **6** and other electrophilic olefins failed owing to decomposition of the starting ylide **6** under the reaction conditions.



(6)

The 2,3-sigmatropic rearrangement of an allyl sulfonium ylide was briefly investigated.[13] 1-Allyl-thioniacyclohexan-3-one perchlorate (**21**) was prepared from thiacyclohexan-3-one,[14] and allyl bromide in the presence of $AgClO_4$. Treatment of **21** with sodium methoxide in methanol at 0°C for 1 h gave 2-allyl-thiacyclohexan-3-one in 53% overall yield (Eq. (7)).

21 **22** (7)

EXPERIMENTAL

2-Methyl-4-oxo-isothiochromanium perchlorate (**1a**). Isothiochroman-4-one[15] (5.0 g, 31 mmol) was added to a magnetically stirred solution of $AgClO_4$ (6.30 g, 31 mmol) in 50 mL of dry acetonitrile at − 5° to 0°C and the mixture was stirred for 10 min. Iodomethane (22 g, 155 mmol) in 10 mL of dry acetonitrile was then added, and the reaction mixture was stirred at 0°C for 3 h. TLC analysis showed the disappearance of the starting sulfide after 1 h. The resultant suspension was filtered and the solvent was evaporated to give sulfonium salt **1a**, which was recrystallized from acetonitrile to give 7.7 g (90%) of **1a** as a pale yellow crystalline solid: mp 198–199°C; ^1H NMR ($(CD_3)_2SO$) δ 7.76 (m, 4 H), 4.70 (d of q, J = 18 Hz, 4 H, CH_2), 2.85 (s, 3 H, SCH_3); IR (KBr) 1683 (C=O), 1080 (ClO_4^-) cm^{-1}. Anal. Calcd for $C_{10}H_{11}O_5SCl$: C, 43.09; H, 3.98; S, 11.51. Found: C, 42.96; H, 4.15; S, 11.52.

2,3-Dimethyl-4-oxo-isothiochromanium perchlorate (**2**). A solution of 2-methyl-isothiochroman-4-one[12] (3.3 g, 17 mmol) in 50 mL of dry acetonitrile was added to a stirred solution of $AgClO_4$ (3.5 g, 17 mmol) in 50 mL of dry acetonitrile at 0°C. After 10 min, a solution of iodomethane (12 g, 85 mmol) in 10 mL of dry acetonitrile was added. The solution was stirred at 0°C for 24 h, and the resultant yellow precipitate of AgI was removed by filtration. The solvent was evaporated and the residue was recrystallized from acetonitrile to give 4.70 g (95%) of **2** as a mixture of diastereomers: mp 138–140°C; ^1H NMR (CD_3CN) δ 8.10 (m, 1 H), 7.60 (m, 3 H), 4.90 (m, 3 H), 3.00 and 2.70 (s, total 3 H, SCH_3), 1.75 and 1.65 (d, J = 7.5 Hz, total 3 H, CH_3); IR (KBr) 1680 (C=O), 1590, 1075 (ClO_4^-) cm^{-1}. Anal. Calcd for $C_{11}H_{13}O_5SCl$: C, 45.13; H. 4.48; S, 10.95. Found: C, 44.92; H, 4.35; S, 11.15.

1-Methyl-thioniacyclohexan-3-one perchlorate (**3**). A solution of $AgClO_4$ (3.6 g, 17 mmol) and dry acetonitrile (50 mL) was cooled to 0°C and a solution of thiacyclohexan-3-one[14] (2.0 g, 17 mmol) in 20 mL of dry acetonitrile was added dropwise. After the addition was complete, the solution was stirred for 10 min. A solution of iodomethane (12.5 g, 88 mmol) in dry acetonitrile (20 mL) was then added. The reaction mixture was stirred for 4 h at 0°C, and for 24 h at room temperature. The resultant suspension was filtered, the solvent was removed in vacuo, and the residue was washed with dry ether to remove the starting materials. The product was obtained as a white hygroscopic solid (3.73 g, 95%); mp 123–125°C; ^1H NMR (CD_3CN) δ 3.95 (q, J = 14 Hz, 2 H), 3.00–3.95 (m, 2 H), 2.90 (s, 3 H, SCH_3), 1.60 (m, 4 H), IR (KBr) 1716 (C=O), 1412, 1075 (ClO_4^-) cm^{-1}. Anal. Calcd for $C_6H_{11}O_5SCl$: C, 31.24; H, 4.81; S, 13.90. Found: C, 31.20; H, 4.68; S, 13.65.

2,3-Dimethyl-1(4H)-3-thianaphthalenone (**5**). A solution of sulfonium salt **2** (2.93 g, 10 mmol) and sodium (2.23 g, 10 mmol) in 60 mL of dry methanol was stirred at 0° to −5°C. The mixture was concentrated to give a residue which was recrystallized from acetonitrile to give 1.52 g (79%) of a yellow crystalline solid: mp 149–151°C; ^1H NMR ($CDCl_3$) δ 7.95 (m, 1 H), 7.15 (m, 3 H), 4.08 (q, J = 16 Hz, 2 H, CH_2), 2.30 (s, 3 H, SCH_3), 1.98 (s, 3 H, CH_3); IR (KBr) 1500 (C=O), 1393, 1355, 955 cm^{-1}. Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29; S, 16.67. Found: C, 68.63; H, 6.39; S, 16.45.

2-[1,2-(Dimethoxycarbonyl)ethenyl]-3-methyl-1(4H)-3-thianaphthalenone (**7**). Sulfonium salt **1a** (2.8 g, 10 mmol) was added to a solution of sodium (0.23 g, 10 mmol) in 50 mL of methanol at 0°C. A solution of dimethyl acetylenedicarboxylate (7.1 g, 50 mmol) in 20 mL of dry methanol was then added to the ylide solution, and the entire mixture was stirred for 14 h at 0°C. The precipitate was collected by filtration and recrystallized from acetonitrile to give 2.30 g (72%) of **7** as a yellow crystalline solid: mp 212°C (dec.); ^1H NMR ($(CD_3)_2SO$) δ 7.90 (m, 1 H), 7.45 (m, 3 H), 6.25 (s, 1 H), 4.70 (q, J = 16 Hz, 2 H), 3.75 (s, 3 H, OCH_3), 3.55 (s, 3 H, OCH_3), 2.50 (s, 3 H, SCH_3); IR (KBr) 1730, 1700, 1563 (C=C), 1512 (ylide C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_5S$: C, 59.99; H, 5.04. Found: C, 60.22; H, 4.97. MS *m/e* 320 (M^+).

2-(1,2,2-Tricyanoethenyl)-3-methyl-1(4H)-3-thianaphthalenone (**8**). A solution of tetracyanoethylene (0.70 g, 5.5 mmol) in 50 mL of dry methanol was added to a magnetically stirred solution of ylide **4** (0.90 g, 5.1 mmol) in 20 mL of dry methanol at 0°C. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for 30 min. The resultant suspension was filtered, and washed with 20 mL of acetone to give 1.0 g (71%) of **8** as a pale yellow crystalline solid: mp 226–228°C (dec.); ^1H NMR ($(CD_3)_2SO$) δ 8.09 (m, 1 H), 7.68 (m, 3 H), 4.83 (q, J = 16 Hz, 2 H), 2.80 (s, 3 H); IR (KBr) 2200 (CN), 1616 (C=C), 1457, 1369, 1270 cm^{-1}. Anal. Calcd for $C_{15}H_9N_3OS$: C, 64.50; H, 3.25; N, 15.04; S, 11.48. Found: C, 64.55; H, 3.25; N, 14.91; S, 11.41.

2-Acetyl-3-methyl-1(4H)-3-thianaphthalenone (**9**). Acetic anhydride (1.10 g, 11 mmol) was added to a stirred solution of ylide **4** (prepared from sulfonium salt **1a** (2.80 g, 10 mmol)) in 20 mL of dichloromethane at 0°C. The reaction mixture was slowly warmed to room temperature and stirred for 10 h. The resultant precipitate was collected by filtration and recrystallized from ethanol to afford 0.30 g (14%) of **9** as a colorless crystalline solid: mp 191.5–192.5°C; ^1H NMR ($(CD_3)_2SO$) δ 8.09 (m, 1 H), 7.55 (m, 3 H), 4.58 (q, J = 16 Hz, 2 H), 2.43 (s, 3 H, CH_3), 2.35 (s, 3 H, SCH_3); IR (KBr) 1569, 1536 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.43; H, 5.49; S, 14.55. Found: C, 65.70; H, 5.48; S, 14.24.

6-[2-(Methylthiomethyl)phenyl]-3,4-diphenyl-2H-pypan-2-one (**10**). Into a solution of ylide **4** in 50 mL of methanol prepared from sulfonium salt **1a** (2.80 g, 10 mmol) was added a solution 2,3-diphenyl-2-cyclopropen-1-one (**12**)[16] (2.10 g, 10 mmol) at room temperature. After the reaction mixture was stirred for 18 h, the resultant precipitate was collected by filtration and recrystallized from ethanol afforded 1.90 g (50%) of **10** as a pale yellow crystalline solid: mp 129.5–130.5°C; ^1H NMR (CCl_4) δ 7.28 (m, 14 H), 6.60 (s, 1 H), 4.00 (s, 2 H, SCH_2) 2.04 (s, 3 H, SCH_3); IR (KBr) 1717 (C=O), 1628 (C=C), 1534 (C=C) cm^{-1}; MS *m/e* 384 (M^+). Anal. Calcd. For $C_{25}H_{20}O_2S$: C, 78.10; H, 5.24; S, 8.34. Found: C, 77.83; H, 5.03; S, 8.64.

6-[2-(Methylthiomethyl)phenyl]-3,4-diphenyl-2H-pyran-2-thione (**11**). A solution of 2,3-diphenyl-2-cyclopropene-1-thione[17] (3.00 g, 5.9 mmol) in 50 mL of methanol was added dropwise at 0°C to a solution of **4** (5.7 mmol) in 40 mL of methanol. The solution was stirred for 24 h at 0°C. Evaporation in vacuo yielded a crude product which was recrystallized from acetone gave 1.20 g (53%) of **11** as a red crystalline solid: mp 142.5–143.5°C; ^1H NMR ($CDCl_3$) δ 7.27 (m, 14 H), 6.93 (s, 1 H), 4.15 (s, 2 H, SCH_2), 2.10 (s, 3 H, SCH_3); IR (KBr)[18] 1619, 1507, 1475, 1336, 1249, 1107 cm^{-1}. Anal. Calcd for $C_{25}H_{20}OS_2$: C, 74.97; H, 5.03; S, 16.01. Found: C, 74.76; H, 4.89; S; 15.86.

5-Methyl-6-[2-(methylthiomethyl)phenyl)]-3,4-diphenyl-2H-pyran-2-one (**14**). To a solution of ylide **5**, prepared from sulfonium salt **2** (2.93 g, 10 mmol) and sodium (0.23 g, 10 mmol) in 70 mL of methanol at 0°C, was added 2,3-diphenyl-2-cyclopropen-1-one (**12**)[17] (2.00 g, 10 mmol). After the addition was complete, the mixture was stirred at room temperature for 48 h. Evaporation of the solvent gave a solid which was recrystallized from acetone to give 3.00 g (75%) of **14** as colorless plates: mp 151.5–152.5°C; ^1H NMR ($CDCl_3$) δ 7.40 (m, 4 H), 7.15 (m, 10 H), 3.78 (s, 2 H, SCH_2), 1.98 (s, 3 H, SCH_3), 1.64 (s, 3 H, CH_3); IR (KBr) 1708 (C=O), 1628 (C=C), 1535 (C=C) cm^{-1}; MS *m/e* 398 (M^+), 351 (M^+-SCH_3). Anal. Calcd for $C_{26}H_{22}O_2S$: C, 78.36; H, 5.57; S, 8.04. Found: C, 78.18; H, 5.54; S, 8.05.

5-Methyl-6-[2-(methylthiomethyl)phenyl]-3,4-diphenyl-2H-pyran-2-thione (**15**). To a solution of ylide **5** in 50 mL of methanol (prepared from sulfonium salt **2** (1.47 g, 5 mmol) and sodium (0.12 g, 5 mmol)) was added **13** (1.11 g, 5 mmol) at room temperature. After stirring for 48 h, the mixture was evaporated to give a solid (1.38 g, 66%), which was recrystallized from methanol to yield a red crystalline solid: mp 145–148°C; ^1H-NMR ($CDCl_3$) δ 7.20 (m, 4 H), 6.95 (m, 10 H), 3.80 (s, 2 H, SCH_2), 1.98 (s, 3 H, SCH_3), 1.65 (s, 3 H, CH_3); IR (KBr)[18] 1620 (C=C), 1470, 1270, 1150 (C=S), 1110 cm^{-1}. MS *m/e* 414 (M^+), 367 (M^+-SCH_3). Anal. Calcd for $C_{22}H_{22}OS_2$: C, 75.33; H, 5.35; S, 15.47. Found: C, 75.39; H, 5.45; S, 15.52.

6-[3-(Methylthio)propyl)]-3,4-diphenyl-2H-pyran-2-one (**17**). A solution of sulfonium salt **3** (2.30 g, 11 mmol) and dry methanol (20 mL) was cooled to −78°C and sodium methoxide (11 mmol) was added. After 10 min, a solution of **12** (2.10 g, 10 mmol) in 50 mL in dry methanol was added. The reaction mixture was stirred for 24 h with slow warming to room temperature. Removal of solvent in vacuo and chromatography on silica gel (chloroform as an eluent) gave a white solid, which was recrystallized from ethanol to give 2.07 g (57%) of **17**: mp 78–79°C; ^1H NMR (CCl_4) δ 7.22 (m, 10 H), 6.16 (s, 1 H), 2.65 (m, 4 H), 2.12 (s, 3 H, SCH_3); IR (KBr) 1703 (C=O), 1642 (C=C), 1544 (C=C) cm^{-1}. Anal. Calcd for $C_{21}H_{20}O_2S$: C, 74.97; H, 5.99; S, 9.53. Found: C, 75.19; H, 6.01; S, 9.37.

6-[3-(Methylthio)propyl]-3,4-diphenyl-2H-pyran-2-thione (**18**). A solution of sulfonium salt **3** (1.15 g, 5 mmol) and dry methanol (5 mL) was cooled to 0°C and sodium methoxide (0.27 g, 5 mmol) was added. After 20 min, a solution of **13** (1.11 g, 5 mmol) in 10 mL of dry methanol and 5 mL of dry acetone was added. After the addition was complete, the mixture was stirred for 48 h at room temperature. Evaporation of the solvent and recrystallization from methanol gave a brick-red crystalline solid (1.40 g, 79%): mp 123.5–124.5°C; ^{1}H NMR ($CDCl_3$) δ 6.90–7.20 (m, 10 H), 6.40 (s, 1 H), 2.50–2.90 (m, 4 H), 2.10 (m, 5 H, SCH_3 + CH_2); IR (KBr) 1628 (C=C), 1260, 1105 (C=S) cm^{-1}. MS *m/e* 352 (M^+). Anal. Calcd for $C_{21}H_{20}OS_2$: C, 71.55; H, 5.72; S, 18.19. Found: C, 71.47; H, 5.75; S, 17.89.

3-Benzoyloxy-1-methyl-thioniacyclohex-2-ene perchlorate (**20**). The ylide **6** was prepared from sulfonium salt **3** (2.30 g, 10 mmol) and sodium methoxide (10 mmol) in 20 mL of dry methanol. Evaporation of the solvent under vacuum gave a brown oil which was dissolved in dry acetone. Benzoyl chloride (1.40 g, 10 mmol) was then added at room temperature with stirring. After 18 h, the mixture was stripped of most of the solvent, and the residual solid was recrystallized from acetone (1.65 g, 49%): mp 174–176°C; ^{1}H NMR (CD_3CN) δ 7.50–8.10 (m, 5 H), 6.50 (s, 1 H), 3.40–3.60 (m, 2 H), 3.00 (s, 3 H, SCH_3), 2.50–2.80 (m, 4 H, $2CH_2$); IR (KBr) 1742 (C=O), 1236 (COO), 1110 (ClO_4^-) cm^{-1}. MS *m/e* 220, 122. Anal. Calcd for $C_{13}H_{15}O_6SCl$: C, 46.64; H, 4.52; S, 9.58. Found: C, 46.90; H, 4.78; S, 9.56.

Rearrangement of Sulfonium Ylide **6**. Thiacyclohexan-3-one (3.00 g, 26 mmol) was mixed with $AgClO_4$ (5.4 g, 26 mmol) and 60 mL of dry acetonitrile at 0°C. Then allyl bromide (3.50 g, 26 mmol) was added, and the reaction mixture was stirred at 0°C to room temperature for 48 h. The resulting precipitates were removed by filtration (80% of AgBr). Evaporation of the solvent in vacuo gave an oil. Methanol (60 mL) was added to this oil and then sodium methoxide (22 mmol) in methanol was added at 0°C. The mixture was allowed to stir 1 h at 0°C. The mixture was diluted with water and extracted three times with ether. The combined ethereal extracts were dried with Na_2SO_4 and concentrated to give an oil. GLC analysis using *p*-nitrotoluene as internal standard gave 53% yield of 2-allyl-thiacyclohexan-3-one (**22**).

Chromatography on silica gel with benzene gave an analytical sample: bp 130°C/27 mmHg; ^{1}H NMR (CCl_4) δ 5.80 (m, 1 H), 5.00 (m, 2 H), 3.40 (t, J = 6.5 Hz, 1 H), 2.00–3.05 (m, 8 H). Anal. Calcd for $C_8H_{12}OS$: C, 61.50; H, 7.74; S, 20.52. Found: C, 61.11; H, 7.73; S, 20.22.

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