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The Reaction of Thio-substituted Cyclopropenium Ions with Sulfonium Methylide

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The reaction between thio-substituted cyclopropenium ions and sulfonium methylides gives unanticipated ketene derivatives. This reaction is supposed to proceed through an intermediate sulfonium salt formed from ylide addition to the cyclopropenyl ring.

Recently, interest has focused on the hetero-atom-substituted three-membered rings because of their highly strained character, and a number of interesting reactions have been reported.[1,2] Among them, a variety of reactions of nitrogen-atom-substituted cyclopropenium compounds were studied.[3] We have recently reported the formation of both cyclopropenimines and *N*,*N*′-dicyclopropenylidenureas.[4] In reactions of nitrogen-atom-substituted cyclopropenium ions with ylides, ring-opened products were not detected and they were supposed to arise exclusively from the nucleophilic substitution reaction. In this paper, we shall describe the reaction[5] between thio-substituted cyclopropenium ions and sulfonium methylide, and an elucidation of the reaction mechanism.

Results and Discussion

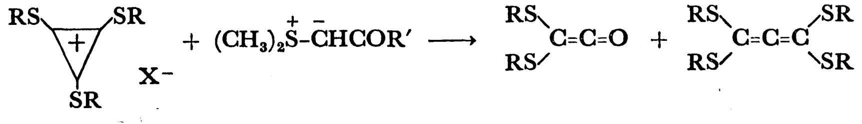
When a mixture of **1a** and **2a** (molar ratio of 1 to 4) in THF was treated at room temperature for 8 h under He atmosphere, bis(ethylthio)ketene (**3a**) was obtained. The structure of **3a** was established from its spectroscopic data as well as its elemental analysis. It was found to be identical with a compound prepared by the reaction of bis(ethylthio)acetyl chloride with triethylamine according to the method[6] for the preparation of bis(alkylthio)ketene. Consequently the structure **3a** is assigned to the product.

While the reaction of **1b** with **2a** in THF give predominantly or exclusively the product **3b**, a small amount of compound **4b** is also produced. The ^{1}H-NMR spectrum of **4b** was found to be identical with that of tetrakis(*t*-butylthio)allene.[7] We, therefore, have investigated the reaction of **1** with **2** under various conditions, because it is known that the allene may arise *via* a cyclopropenylidene intermediate. A compound formed by the reaction between **1e** and **2a** was identified as **4b**. The expected **4a** was not found in the reaction mixture of **1d** and **2c** in THF although ketene **3a** was given. No tetrakis(*p*-*t*-butylphenylthio)allene, which would be formed along with the corresponding ketenes from reactions of **1c** and **1f** with **2a**, **2b**, and **2c**, was detected. The equation of the reactions between thio-substituted cyclopropenium ions (**1**) and sulfonium methylide (**2**) can be written as in Scheme 1.

The conditions employed for obtaining **3a** in the preliminary work can be applied to the reactions of other thio-substituted cyclopropenium ions. These results are summarized in Table 1. The generation of **3** from the reaction between thio-substituted cyclopropenium ions and sulfonium methylides showed that the original ylide-carbonyl oxygen remains intact in the ketene. This ketene skeleton seems to be composed of the ylide carbon and the ylide-carbonyl group.

All attempts to produce allenes by the reactions of **1a**, **1e**, **1d**, and **1f** and **2a**—**c** have failed. The ketenes were the only products obtained.

When the reaction of **1a** with **2a** (molar ratio of 1 to 1) was carried out in THF at −5 °C for 8 h under He atmosphere, [[tris(ethylthio)cyclopropenyl](ethoxycarbonyl)methyl]dimethylsulfonium perchlorate (**5a**) was isolated in 7.5% yield, along with **3a**. The structure of **5a** was inferred on the basis of the results of



1 **2** **3** **4**

2a: $R'=CH_3CH_2O$-
2b: $R'=C_6H_5$-
2c: $R'=CH_3CH_2S$-

	R	X^-
1a:	CH_3CH_2-	ClO_4
1b:	$(CH_3)_3C$-	ClO_4
1c:	*p*-$(CH_3)_3C$-C_6H_4-	ClO_4
1d:	CH_3CH_2-	BF_4
1e:	$(CH_3)_3C$-	BF_4
1f:	*p*-$(CH_3)_3C$-C_6H_4-	BF_4

3a $R=CH_3CH_2$-
3b: $R=(CH_3)_3C$-
3c: $R=$*p*-$(CH_3)_3C$-C_6H_4-

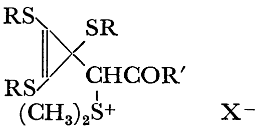
4a: $R=CH_3CH_2$-
4b: $R=(CH_3)_3C$-
4c: $R=$*p*-$(CH_3)_3C$-C_6H_4-

Scheme 1. The reaction of thio-substituted cyclopropenium ions with sulfonium methylide.

Table 1. Conditions and yields for reactions of **1a**—**f** with **2a**—**c**

Substrate	Reagent	Solvent	Temp	Time/h	Products/%
1a	**2a**	THF	RT	8	**3a** (61)
1a	**2b**	THE	RT	8	**3a** (53)
1b	**2a**	THF	RT	8	**3b** (87) **4b** (10)
1b	**2b**	THF	RT	8	**3b** (54)
1c	**2a**	THF	RT	8	**3c** (66)
1c	**2b**	THF	RT	8	**3c** (61)
1d	**2a**	THF	RT	6	**3a** (33)
1d	**2c**	THF	RT	6	**3a** (65)
1e	**2a**	THF	RT	6	**3b** (40) **4b** (11)
1e	**2c**	THF	RT	6	**3b** (70)
1f	**2a**	THF	RT	6	**3c** (56)
1f	**2c**	THF	RT	6	**3c** (62)

Table 2. Sulfonium salts



Compd	R	R′	X−	Yield %	Mp θ_m/°C	Fomula	Found(%) C	Found(%) H	Calcd(%) C	Calcd(%) H
5a	CH_3CH_2-	CH_3CH_2O-	ClO_4	64	168—170	$C_{15}H_{27}O_6S_4Cl$	38.50	5.82	38.57	5.83
5b	CH_3CH_2-	CH_3CH_2S-	ClO_4	72	190—192	$C_{15}H_{27}O_5S_5Cl$	37.25	5.61	37.29	5.63
5c	$(CH_3)_3C$-	CH_3CH_2O-	ClO_4	45	171—173	$C_{21}H_{39}O_6S_4Cl$	45.68	7.01	45.76	7.13
5d	$(CH_3)_3C$-	CH_3CH_2S-	ClO_4	33	167—169	$C_{21}H_{39}O_5S_5Cl$	44.48	6.89	44.60	6.93
5e	*p*-$(CH_3)_3C$-C_6H_4-	CH_3CH_2O-	ClO_4	57	182—183	$C_{39}H_{51}O_6S_4Cl$	59.98	6.50	60.09	6.60
5g	CH_3CH_2-	CH_3CH_2O-	BF_4	26	163—164	$C_{15}H_{27}O_2S_4BF_4$	39.95	5.94	39.64	5.99
5h	CH_3CH_2-	CH_3CH_2S-	BF_4	59	192—195	$C_{15}H_{27}OS_5BF_4$	38.21	5.75	38.29	5.78
5i	$(CH_3)_3C$-	CH_3CH_2O-	BF_4	27	170—172	$C_{21}H_{39}O_2S_4BF_4$	46.81	7.26	46.83	7.30
5j	$(CH_3)_3C$-	CH_3CH_2S-	BF_4	29	160—162	$C_{21}H_{39}OS_5BF_4$	45.42	6.99	45.47	7.09

the elemental analysis as well as its ^{1}H-NMR spectrum which has a methyl-singlet at δ 3.15 (6H) and ethyl-signals at δ 1.50 (9H, t), 3.05 (4H, q), and 4.18 (2H, q) in addition to signals for ester group at δ 1.35 (3H, t) and 3.40 (2H, q). Under similar conditions, [[tris(*t*-butylthio)cyclopropenyl]-(**5c**) and [[tris(*p*-*t*-butylphenylthio)cyclopropenyl](ethoxycarbonyl)methyl]dimethylsulfonium perchlorates (**5e**) were isolated in 4.8 and 7.3% yields, respectively.

Likewise, **1d** reacts with **2a** and **2c** in THF at 0 °C for 6 h giving [[tris(ethylthio)cyclopropenyl](ethoxycarbonyl)methyl]dimethylsulfonium tetrafluoroborate (**5g**) and [[tris(ethylthio)cyclopropenyl](ethylthiocarbonyl)methyl]dimethylsulfonium tetrafluoroborate (**5h**), respectively.

Thus, an attempt was made to prepare the sulfonium intermediate **5** by the nucleophilic addition reaction. When the reaction of **1a** with **2a** (molar ratio of 1 to 1) was performed in dry THF at −40 °C for 6 h under He atmosphere, the sulfonium salt **5a** was obtained in good yield. Similarly, reactions of **1b**—**e** with **2a** and **2c** gave the corresponding sulfonium salts, such as [[tris(ethylthio)cyclopropenyl]-(ethylthiocarbonyl)methyl]dimethylsulfonium perchlorate (**5b**), **5c**, [[tris(*t*-butylthio)cyclopropenyl](ethylthiocarbonyl)methyl]dimethylsulfonium perchlorate (**5d**), **5e**, **5g**, **5h**, [[tris(*t*-butylthio)cyclopropenyl](ethoxycarbonyl)methyl]dimethylsulfonium tetrafluoroborate (**5i**), and [[tris(*t*-butylthio)cyclopropenyl](ethylthiocarbonyl)methyl]dimethylsulfonium tetrafluoroborate (**5j**). However, no sulfonium salt, which would be formed from the reaction of **1f**, was detected. Results are summarized in Table 2. The structures of the sulfonium salts **5** were determined by elemental analyses, ^{1}H-NMR spectroscopic data and IR spectra (showing the three-membered ring and $\rangle$C=O stretching bands). These results strongly suggest that the reaction of cyclopropenium ions with sulfonium ylides proceeds *via* sulfonium salts, nucleophilic addition products.

The structure of **5** permit us to indicate a possible reaction pathway. The reaction should involve, as the first step, nucleophilic attack of ylide carbanion by ring-carbon. Thus the sulfonium salt formation from thio-substituted cyclopropenium ions can occur with sulfonium methylides. Then the sulfonium salts with an appropriate leaving group SR and $(CH_3)_2S^+$ may be subject to elimination of $(CH_3)_2S^+$, intramolecular rearrangement of SR and ring opening to give the ketene **3**. The allene **4** may arise from a cyclopropenylidene intermediate, generated by elimination of a ketene moiety from **5**. Although we do not believe

TABLE 3. PHYSICAL DATA OF SULFONIUM SALTS (**5**)

5	^{1}H-NMR: δ ($CDCl_3$)	IR$^{a)}$ $\tilde{\nu}$/cm^{-1}		UV$^{b)}$ λ_{max}/nm (ε)
		▽	C=O	
5a	1.35 (3H, t), 1.50 (9H, t), 3.05 (4H, q) 3.15 (6H, s), 3.40 (2H, q), 4.18 (2H, q)	1800	1670	270 (14000), 280 (12000)
5b	1.22 (3H, t), 1.40 (9H, t), 2.90 (2H, q) 3.08 (6H, s), 3.20 (4H, q), 3.45 (2H, q)	1790	1630	244 (8300), 282 (7000) 306 (10000)
5c	1.37 (3H, t), 1.53 (9H, s), 1.68 (18H, s) 3.18 (6H, s), 4.23 (2H, q)	1780	1670	272 (10900), 285*(9100)
5d	1.30 (3H, t), 1.55 (9H, s), 1.68 (18H, s) 2.95 (2H, q), 3.22 (6H, s)	1770	1640	244 (9000), 282*(7000) 306 (11000)
5e	1.29 (27H, s), 1.45 (3H, t), 2.82 (6H, s) 4.25 (2H, q), 7.65 (12H, d)	1800	1680	274 (10000)
5g	1.35 (3H, t), 1.50 (9H, t), 3.05 (4H, q) 3.15 (6H, s), 3.40 (2H, q), 4.18 (2H, q)	1800	1670	270 (33000), 281*(28000)
5h	1.22 (3H, t), 1.40 (9H, t), 2.90 (2H, q) 3.08 (6H, s), 3.20 (4H, q), 3.45 (2H, q)	1780	1630	243 (17000), 281*(14000) 306 (22000)
5i	1.37 (3H, t), 1.53 (9H, s), 1.68 (18H, s) 3.18 (6H, s), 4.23 (2H, q)	1790	1690	274 (35000), 286*(13000)
5j	1.30 (3H, t), 1.55 (9H, s), 1.68 (18H, s) 2.95 (2H, q), 3.22 (6H, s)	1760	1620	248 (15000), 308 (17000)

a) Measured in KBr disk. b) Observed in CH_3CN. * Shoulder.

that the limited data available here can permit us to discuss a further precise mechanism, the present results strongly support the intermediacy of the sulfonium salt such as **5** in reactions between the thio-substituted cyclopropenium ion system and sulfonium methylide.

Experimental

All the melting points are uncorrected. The IR spectra were taken with a Hitachi Model 215 spectrophotometer; the UV spectra with a Hitachi Model EPS-3T spectrometer; and the ^{1}H-NMR spectra with a JEOL Model JNM-C-60H spectrometer. The chemical shifts are expressed in parts per million downfield from internal tetramethylsilane (δ=0). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All the reactions were carried out under He atmosphere unless otherwise noted.

Materials. The sulfonium methylides **2a**—**c** were synthesized according to reported procedures[8] and identified by elemental analyses and melting points as well as by comparison of IR. The syntheses of thio-substituted cyclopropenium perchlorates (X=ClO_4, **1a**—**c**) were reported previously.[4,9]

*Tris(ethylthio)cyclopropenium Tetrafluoroborate (**1d**).* To a stirred of tetrachlorocyclopropene (91.6 mmol) in boron trifluoride (abt 49%, 40 g), there was added ethanethiol (36.6 mmol), dropwise, at room temperature. The mixture was stirred under reflux for 3 h. It was then cooled to room temperature, poured into ice-water, and extracted with dichloromethane. The organic layer was dried over $MgSO_4$, stripped of solvent, washed with ether, and dried under reduced pressure to give yellow crystals (**1d**) in 63% yield; mp 107—109 °C; UV$_{max}$ (CH_3OH) 272 nm (ε 3100); IR (KBr) 1250 and 1090 cm^{-1}. Found: C, 35.19; H, 4.82%. Calcd for $C_9H_{15}S_3BF_4$: C, 35.30; H, 4.94%.

*Tris(*t*-butylthio)- (**1e**) and Tris(*p-t*-butylphenylthio)cyclopropenium Tetrafluoroborates (**1f**).* In a similar manner to the above, **1e** and **1f** were prepared from the corresponding thiols in 42 and 50% yields, respectively. **1e**: yellow crystals; mp 129—131 °C; UV$_{max}$ (CH_3OH) 272 nm (ε 3570); IR (KBr) 1250 and 1090 cm^{-1}. Found: C, 46.02; H, 7.04%. Calcd for $C_{15}H_{27}S_3BF_4$: C, 46.15; H, 6.97%. **1f**: Colorless needles; mp 149—152 °C; UV max (CH_3OH) 250 (ε 4300) and 275 nm (3600); IR (KBr) 1250 and 1090 cm^{-1}. Found: C, 64.27; H, 6.03%. Calcd for $C_{33}H_{39}S_3BF_4$: C, 64.27; H, 6.35%.

*Reaction of Thio-substituted Cyclopropenium Ions (**1**) with Sulfonium Methylides (**2**). General Procedure:* A mixture of **1** (10 mmol) and **2** (40 mmol) in dry THF (80 or 100 ml) was stirred at room temperature for 6 or 8 h. After which the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel, eluting with carbon tetrachloride to give **3** and **4**. The following ketenes and allene were prepared by this procedure.

Physical Properties: **3a**: Pale yellow oil; UV$_{max}$ (CH_3OH) 288 nm (ε 6000); IR (neat) 2160 (⟩C=C=O) and 1640 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.25 (6H, t, J=6.8 Hz, CH_3) and 2.75 (4H, q, J=6.8 Hz, CH_2).

3b: Pale yellow oil; UV$_{max}$ (CH_3OH) 251 nm (ε 6700); IR (neat) 2170 (⟩C=C=O) and 1640 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.45 (18H, s, CH_3).

3c: Pale brown oil; UV$_{max}$ (CH_3OH) 251 nm (ε 11000); IR (neat) 2190 (⟩C=C=O) and 1660 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.41 (18H, s, CH_3) and 7.15 (8H, m, phenyl).

4b: Colorless needles; mp 140—141 °C; UV$_{max}$ (CH_3OH) 269 nm (ε 6500); IR (KBr) 1910 (⟩C=C=C⟨) and 1360 cm^{-1}; ^{1}H-NMR (CCl_4) δ=1.45 (36H, s, CH_3). Found: C, 57.90; H, 9.43%. Calcd for $C_{19}H_{36}S_4$: C, 58.01; H, 9.26%.

*Preparation of Sulfonium Salts (**5**). Preparation of **5e** as a Typical Procedure:* The mixture of **1e** (1.58 mmol) and **2a** (1.58 mmol) in dry THF (80—100 ml) was stirred at −40 °C for 6 h. The reaction mixture was filtered off, and the product was recrystallized from $CHCl_3$–CCl_4 (1:1) to give colorless rod-like crystals, [[tris(*p-t*-butylphenylthio)cyclopropenyl](ethoxycarbonyl)methyl]dimethylsulfonium perchlorate (**5e**) (57% yield). Other sulfonium salts were prepared by the similar procedure, but **5a**, **5b**, **5c**, **5d**, **5g**, **5h**, **5i**, and **5j** were purified by recrystallization from ethanol. Physical data of **5** are summarized in Tables 2 and 3.

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