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Acylation of Cyclopropyl-Substituted Alkenes with Complexes Formed by ω-(Ethylthio)alkanoyl Fluorides and Boron Trifluoride*

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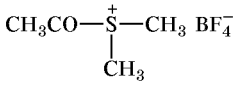
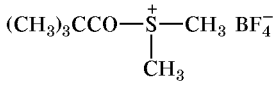
Abstract—Cyclopropyl-substituted alkenes react with complexes formed by boron trifluoride and 3-(ethylthio)propionyl fluoride and 2-(ethylthio)acetyl fluoride to give ketones containing an ethylthio group. In most cases the reaction is not accompanied by opening of the three-membered ring or rearrangements.

Acylation of unsaturated hydrocarbons is a convenient method for synthesis of unsaturated ketones from accessible hydrocarbon raw materials. However, this reaction is often accompanied by polymerization or oligomerization of initial unsaturated hydrocarbons, especially of such reactive alkenes as styrene and conjugated dienes [1, 2].

Modification of strong electrophiles by complex formation with various nucleophiles is one of the main approaches to creation of new electrophilic reagents. Following this approach, complexes of acylium salts with nitriles and acetic anhydride were recently synthesized [3, 4].

We previously found that acylium salts with dimethyl sulfide form complexes which are highly reactive toward various olefins. Using IR and NMR spectroscopy, it was shown that these complexes have the structure of acyldimethylsulfonium salts [5]:





Reactions of acyldimethylsulfonium salts with unsaturated compounds in most cases occur as conjugate addition of the electrophile (acyl group) and nucleophile (dimethyl sulfide) to afford the corresponding sulfonium salts. Subsequent treatment of the reaction mixture with a base leads to formation of α,β-unsaturated ketones (Scheme 1).

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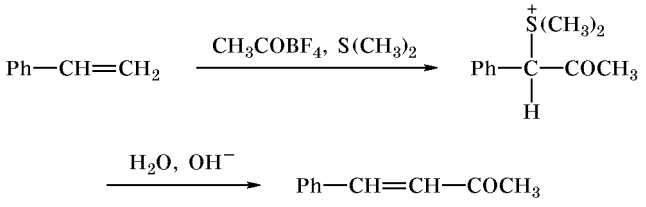
Acyldimethylsulfonium salts smoothly react with readily polymerizable 1,3-dienes, affording the corresponding conjugated dienones in preparative yields. The reaction of $S(CH_3)_2$–BF_3 with trifluoroacetic anhydride gives a complex analogous to acyldimethylsulfonium salts. Its reactions with olefins result in formation of α,β-unsaturated ketones having a trifluoromethyl group [6–11].

Scheme 1.



We recently synthesized intramolecular analogs of acyldimethylsulfonium salts by reactions of ω-(ethylthio)alkanoyl fluorides with boron trifluoride at –60°C. The resulting complexes, as well as acyldimethylsulfonium salts, were found to react with unsaturated hydrocabons to afford conjugate addition products of the acyl and sulfonium moieties at the double bond [12, 13]. We expected that the presence in such complexes of an ethylthio group capable of forming covalent bonds in cationic reactions should suppress side polymerization and isomerization processes which generally accompany acylation of alkenes possessing a three-membered ring. Depending on the acylating agent, the reaction could give cyclopropane and cyclobutane derivatives, products of

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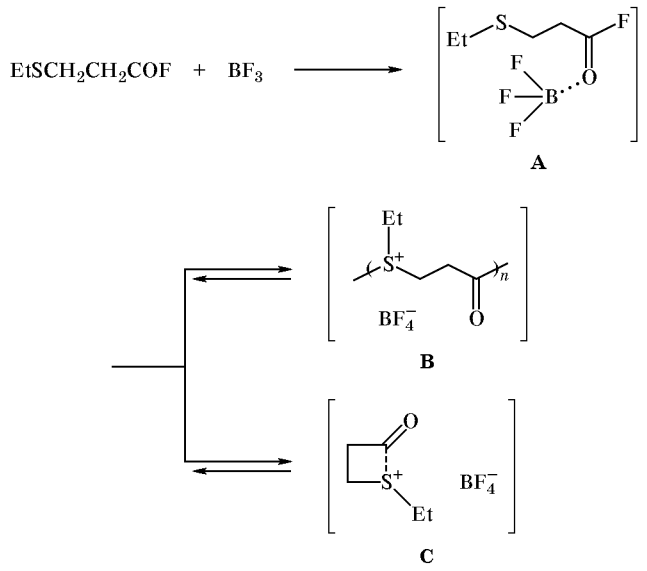
three-membered ring opening, or their mixtures [14–17]. Therefore, cyclopropyl-substituted alkenes are convenient models for studying reactions with ethylthioalkanoyl fluoride–BF_3 complexes and comparing the latter with other acylating agents.

The complexes $EtSCH_2CH_2COF–BF_3$ (**I**) and $EtSCH_2COF–BF_3$ (**II**) were synthesized by saturating a solution of the corresponding acyl fluoride in methylene chloride with boron trifluoride at –60°C. Complex **I** is poorly soluble in methylene chloride and is stable below 0°C. Raising the temperature leads to fast decomposition of the complex into the initial compounds: 3-(ethylthio)propionyl fluoride and boron trifluoride. Complex **II** begins to decompose into the components even at –30°C.

The structure of complexes **I** and **II** was studied by spectral methods. The IR spectra of **I** and **II** at –60°C lacked absorption in the region 2000–2300 cm^{-1}, which is typical of carbonyl group in acylium salts. The presence of absorption bands at 1850 cm^{-1} suggests that the carbonyl group is attached to an acceptor substituent. In the IR spectrum of complex **I** we observed absorption bands at 1710 and 1750 cm^{-1}, which indicate coordination of the BF_3 molecule at the carbonyl oxygen atom.

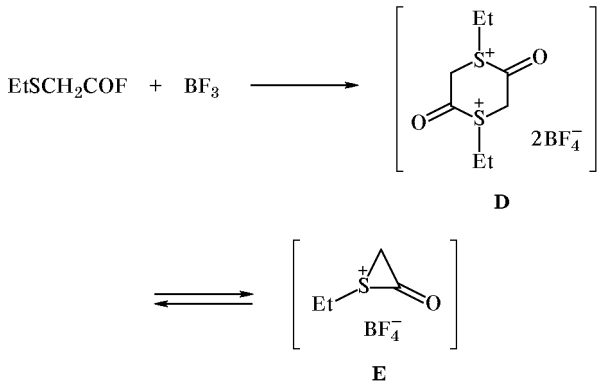
The ^1H and ^{13}C NMR spectra of complex **I** were recorded in a $CD_2Cl_2–C_6D_5NO_2$ mixture (deuterated nitrobenzene was added to increase the solubility) at –60°C. Apart from signals belonging to the initial acyl fluoride, we observed three more sets of signals. The ^{13}C NMR spectrum contained a signal from the carbonyl carbon atom of initial propionyl fluoride as a doublet at δ_C 161.70 ppm with $^1J_{CF}$ = 360 Hz; also, a doublet at δ_C 163.45 ppm ($^1J_{CF}$ = 352 Hz) was present, which is likely to belong to donor–acceptor complex **A**. The singlet at δ 181.93 ppm and broad signal at 180.1–177.4 ppm can be assigned to cyclic form of the complex (**B**) and oligomeric structure **C**, respectively (Scheme 2). The signal from the carbonyl carbon atom (δ_C 181.93 ppm) is not split, indicating formation of a ionic structure with tetrafluoroborate anion. The presence of a positive charge on the sulfur atom is confirmed by downfield shift of signals from the methylene groups attached to the sulfur atom: ^1H: δ 4.1–3.5 ppm against 2.9–2.5 ppm for the initial acyl fluoride; ^{13}C: δ_C 42–36 ppm against 33–24 ppm for the initial acyl fluoride.

Scheme 2.



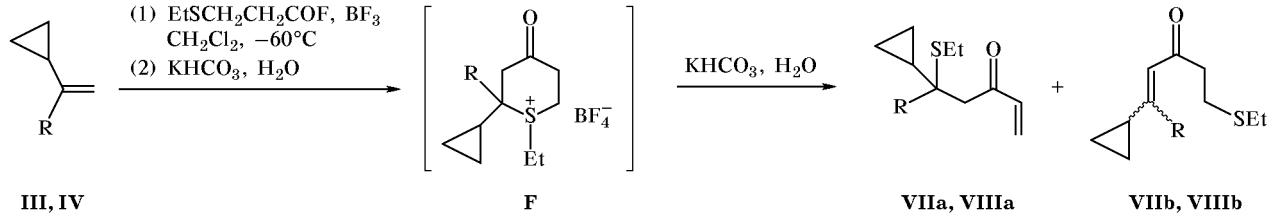
The ^1H and ^{13}C NMR spectra of complex **II** were recorded in CD_2Cl_2 at –55°C. Unlike complex **I**, the spectra of **II** contained no signals from the initial acetyl fluoride $EtSCH_2COF$. According to the NMR data, complex **II** exists in solution as a ~2 : 1 mixture of cyclic dimeric and monomeric forms **D** and **E** (Scheme 3).

Scheme 3.



These structures are characterized by the following sets of signals: **D**: ^1H NMR spectrum, δ, ppm: 4.8–4.6 ($COCH_2$), 3.6–3.35 (CH_2, Et), 1.45–1.35 (CH_3); ^{13}C NMR spectrum, δ_C, ppm: 169.09 (CO), 49.99 (CH_2), 36.74 (CH_2, Et), 10.39(CH_3); **E**: ^1H NMR spectrum, δ, ppm: 4.55–4.45 ($COCH_2$), 3.3–3.15 (CH_2, Et), 1.45–1.35 (CH_3); ^{13}C NMR spectrum: 168.49 (CO), 44.37 (CH_2), 30.48 (CH_2, Et), 11.35 (CH_3). We failed to assign the signals in more detail. The absence of coupling between the carbonyl carbon atom and fluorine indicates that both forms **D** and **E** of complex **II** have ionic structure. As in the spectra of **I**, downfield shift of the methylene group signals in both ^1H and ^{13}C NMR spectra suggests considerable localization of the positive charge on the sulfur atom.

Scheme 4.

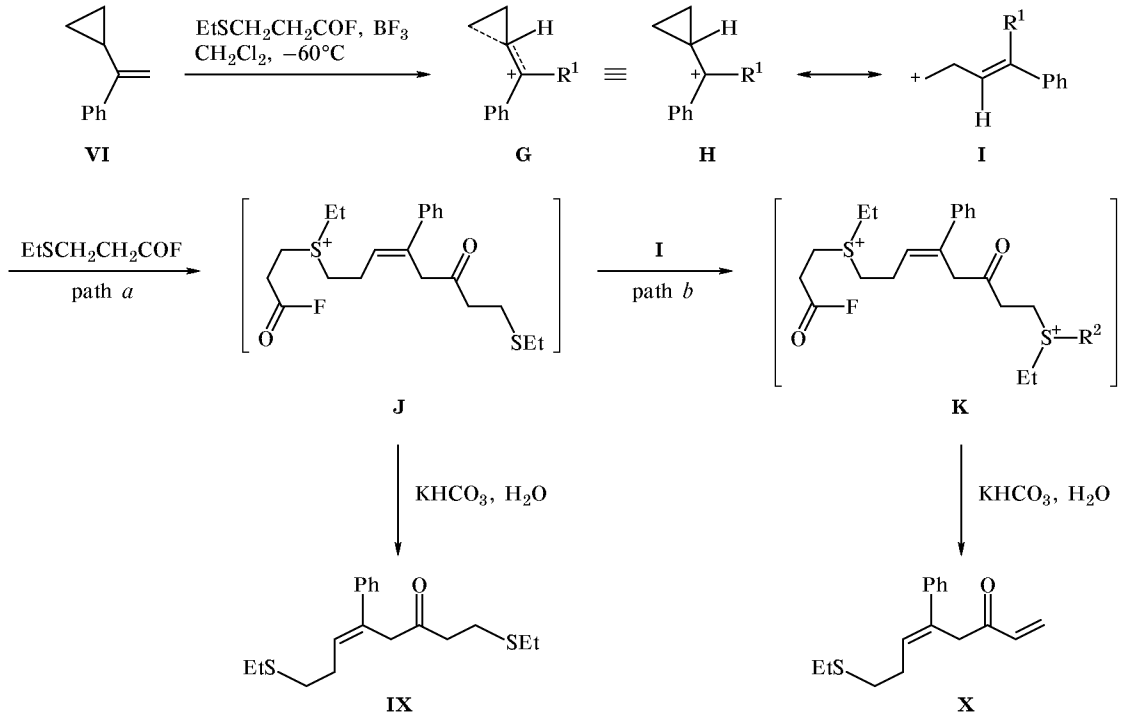


III, **VII**, R = H; **IV**, **VIII**, R = CH_3.

We have examined acylation with the complexes $EtSCH_2CH_2COF–BF_3$ and $EtSCH_2COF–BF_3$ of various hydrocarbons of the vinylcyclopropane series: vinylcyclopropane (**III**), 1-methyl-1-cyclopropylethylene (**IV**), 1,1-dicyclopropylethylene (**V**), and 1-cyclopropyl-1-phenyethylene (**VI**). These reactions were characterized by almost complete suppression of isomerization of the three-membered ring due to binding of intermediate carbocations by the sulfur atom. Opening of the three-membered ring was observed only in the reaction of complex **I** with 1-cyclopropyl-1-phenylethylene (**VI**). In all other cases neither rearrangement nor opening of the three-membered ring occurred (Scheme 4).

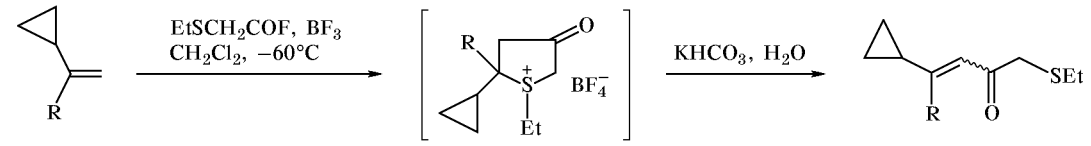
The complex $EtSCH_2CH_2COF–BF_3$ reacted with vinylcyclopropane (**III**) to give a mixture of compounds **VIIa** and **VIIb** at a ratio of 1.2 : 1; here, product **VIIb** was exclusively the *E* isomer. The formation of different α,β-unsaturated ketones can be explained by the fact that intermediate cyclic sulfonium salt **F** reacts with bases along two pathways, affording two possible intramolecular elimination products **VIIa** and **VIIb**. Isopropenylcyclopropane (**IV**) also gives rise to a mixture of products, but the ratio **VIIIa** : *E*-**VIIIb** : *Z*-**VIIIb** is 5 : 1 : 1. In this case, the product ratio **VIIIa** : **VIIIb** is likely to be determined by steric hindrance to elimination. In the reaction of complex **I** with 1-cyclopropyl-1-phenylethylene (**VI**) both

Scheme 5.



R^1 = $CH_2COCH_2CH_2SEt$, R^2 = $(CH_2)_2CH{=}C(Ph)CH_2C(O)(CH_2)_2SEt$.

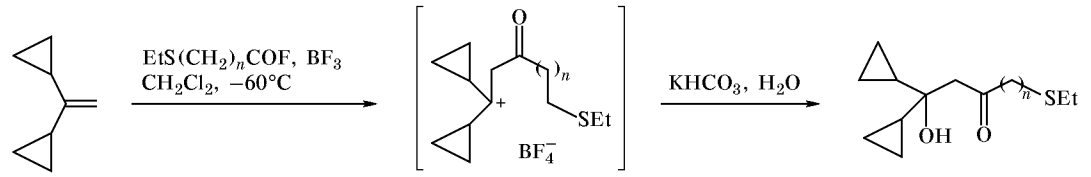
Scheme 6.



III, IV, VI **L** **XI–XIII**

III, **XI**, R = H; **IV**, **XII**, R = Me; **VI**, **XIII**, R = Ph.

Scheme 7.



V **XIV, XV**

XIV, *n* = 1; **XV**, *n* = 2.

products **IX** and **X** were formed via opening of the three-membered ring (Scheme 5), in each case only the *E* isomer being obtained. The double bond configuration at C^5 was determined using NOE spectra. Compounds **IX** and **X** showed no NOE between the vinyl proton on C^6 and CH_2 protons on C^4. On the other hand, NOE for the *ortho*-protons of the benzene ring vinyl proton on C^6 was 5%, which corresponds to the *E* configuration.

The formation of unusual products in the reaction of complex **I** with 1-cyclopropyl-1-phenylethylene (**VI**) may be explained as shown in Scheme 5. First, carbocation **G** is formed, which may be represented by two canonical structures **H** and **I**. Cation **G** can be stabilized via reaction with the sulfur atom of acyl fluoride present in the reaction mixture (path *a*) or via reaction with sulfonium salt thus formed (path *b*). Hydrolysis of sulfonium salts **J** and **K** gives ketones **IX** and **X**, respectively. Unsaturated ketones **IX** and **X** are formed with high stereoselectivity since more bulky phenyl group in intermediate cation **G** occupies the *trans* position relative to the cyclopropane ring.

Reactions of cyclopropyl-substituted hydrocarbons with the complex $EtSCH_2COF–BF_3$ (**II**) were not accompanied by opening or rearrangement of the three-membered ring. The products, α,β-unsaturated ketones **XI**–**XIII**, were obtained in high yields (Scheme 6). The ratio of *E* and *Z* isomers depends on the size of the R radical. When R = Ph (the size of the phenyl group is comparable with that of cyclopropyl), the corresponding *E* and *Z* isomers are formed in equal amounts. In going to R = CH_3, the fraction of the *E* isomer increases, and in the reaction with vinylcyclopropane (R = H) the *E* isomer (**XI**) is formed exclusively.

Complexes **I** and **II** react with 1,1-dicyclopropylethylene (**V**) in an unusual fashion. The only products were β-hydroxyketones **XIV** and **XV**, respectively (Scheme 7).

The formation of such products is likely to be determined by high stability of intermediate dicyclopropylcarbenium ion whose stabilization does not require assistance by sulfur atom. Hydrolysis of the reaction mixture leads to compounds **XIV** and **XV**.

The different paths in reactions of complexes **I** and **II** with 1-cyclopropyl-1-phenylethylene are worth noting. The reaction of **II** with 1-cyclopropyl-1-phenylcyclopropylethylene yields 4-cyclopropyl-1-ethylthio-4-phenyl-3-buten-2-one (**XIII**) as a mixture of *E* and *Z* isomers and involves neither opening nor rearrangement of the cyclopropane ring. An analogous reaction with complex **I** leads to formation of two different ketones **IX** and **X** via opening of the three-membered ring. A probable explanation is that in the reaction of alkene **VI** with complex **II** five-membered cyclic sulfonium salt **L** is rapidly formed, whereas in the reaction with **I** the corresponding six-membered salt **F** is formed at a lower rate, and intermediate carbocation has enough time to undergo rearrangement with opening of the three-membered ring.

Yields, elemental analyses, and IR and NMR spectra of ethylthio-substituted ketones **VII**–**XV**

Compound no.	Yield, %	Found, %		Formula	Calculated, %	
		C	H		C	H
VIIa	34	65.22	8.98	$C_{10}H_{16}OS$	65.17	8.75
VIIb	29	65.31	8.54	$C_{10}H_{16}OS$	65.17	8.75
VIII	45[a]	66.43	8.75	$C_{11}H_{18}OS$	66.62	9.15
IX	19	67.02	8.20	$C_{18}H_{26}OS_2$	67.03	8.13
X	21	73.62	7.69	$C_{16}H_{20}OS$	73.80	7.74
XI	77	63.25	7.98	$C_9H_{14}OS$	63.48	8.29
XII	82[a]	65.25	8.48	$C_{10}H_{16}OS$	65.17	8.75
XIII	49	73.45	7.32	$C_{15}H_{18}OS$	73.13	7.36
XIII	49	73.32	7.39	$C_{15}H_{18}OS$	73.13	7.36
XIV	52	63.53	8.71	$C_{12}H_{20}O_2S$	63.12	8.83
XV	34	64.34	8.84	$C_{13}H_{22}O_2S$	64.42	9.15

Compound no.	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm
VIIa	1690 (C=O), 1620 (C=C)	6.37 d.d (1H, 2-H, ^3J = 17.6, ^3J = 10.4 Hz), 6.20 d.d (1H, 1-H, ^3J = 17.6, ^2J = 1.2 Hz), 5.84 d.d (1H, 1-H, ^3J = 10.4, ^1J = 1.2 Hz), 3.00–2.83 m (2H, $COCH_2$), 2.79–2.48 m (3H, $CHSCH_2$), 1.21 t (3H, CH_3, ^3J 7.2 Hz), 0.95–0.85 m (1H, CH, cyclopropyl), 0.62–0.17 m (4H, $2CH_2$, cyclopropyl)	198.75 (CO), 136.84 (C^2), 128.52 (C^1), 45.99 (C^4), 45.15 (C^5), 25.09 (SCH_2), 17.35 (CH, cyclopropyl), 14.79 (CH_3), 5.41, 4.74 ($2CH_2$, cyclopropyl)
VIIb	1670 (C=O), 1630 (C=C)	6.32 d.d (1H, 1-H, ^3J = 15.6, ^3J = 9.6 Hz), 6.11 d (1H, 2-H, ^3J = 15.6 Hz), 2.77 s (4H, $COCH_2CH_2S$), 2.41 q (2H, $SC\mathbf{H}_2CH_3$, ^3J = 7.6 Hz), 1.62–1.52 m (1H, CH, cyclopropyl), 1.24 t (3H, CH_3, ^3J = 7.6 Hz), 1.00–0.96 m (2H, CH_2, cyclopropyl), 0.68–0.64 m (2H, CH_2, cyclopropyl)	197.65 (CO), 153.26, 126.91 (2HC=), 40.32 (C^4), 26.20, 25.80 (C^3, $S\mathbf{C}H_2CH_3$), 14.75, 14.69 (CH, cyclopropyl, CH_3), 9.08 ($2CH_2$, cyclopropyl)
VIIIa[b]	1680 (C=O), 1600 (C=C)	6.47 d.d (1H, 2-H, ^3J = 17.4, ^3J = 10.4 Hz), 6.20 d.d (1H, 1-H, ^3J = 17.4, ^2J = 1.1 Hz), 5.84 d.d (1H, 1-H, ^3J = 10.4, ^2J = 1.1 Hz), 2.90 d (1H, $COCH_2$, ^3J = 13.5 Hz), 2.81 d (1H, $COCH_2$, ^3J = 13.5 Hz), 2.65 d.q (2H, $SC\mathbf{H}_2CH_3$, ^3J = 7.5, ^2J = 1.2 Hz), 1.22 t (3H, CH_3, ^3J = 7.5 Hz), 1.18 s (3H, CH_3), 0.89–0.70 m (3H, CH, CH_2, cyclopropyl), 0.51–0.33 m (2H, CH_2, cyclopropyl)	198.37 (CO), 137.59 (CH=), 127.60 (=CH_2), 51.03 (C^4), 46.94 (C_{quat}), 26.20, 25.80 (C^3, $S\mathbf{C}H_2CH_3$), 14.75, 14.69 (CH, cyclopropyl, CH_3), 9.08 ($2CH_2$, cyclopropyl)
E-**VIIIb**		6.12 br.s (1H, =CH), 2.83–2.68 m (4H, $COCH_2CH_2S$), 2.56 q (2H, $SC\mathbf{H}_2CH_3$, ^3J = 7.4 Hz), 1.94 d (3H, CH_3C=, ^4J = 1.2 Hz), 1.26 t (3H, CH_3, ^3J = 7.4 Hz); the other signals are overlapped by those of **VIIIa**	Mixture of *Z*-**VIIIb** and *E*-**VIIIb**: 198.49, 197.72 (CO), 161.29, 160.88 (C_{quat}), 123.79, 120.82 (CH=), 44.22, 44.05 (C^2), 26.01, 25.74, 25.72, 22.06 (CH_2SCH_2 and CH_3, allyl), 20.28, 18.61 (CH, cyclopropyl), 15.08, 14.38 (CH_3), 7.20, 7.03 (CH_2, cyclopropyl)

Table. (Contd.)

Compound no.	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm
***Z*-VIIIb**		2.83–2.68 m (4H, $COCH_2CH_2S$), 2.56 q (2H, $SC\mathbf{H}_2CH_3$, ^3J = 7.4 Hz), 1.53 d (3H, $CH_3C=$, ^4J = 1.2 Hz), 1.27 t (3H, CH_3, ^3J = 7.4 Hz); the other signals are overlapped by those of isomer **VIIIa**	
IX	1720 (C=O)	7.31–7.25 m (5H, H_{arom}), 6.00 t (1H, CH=, ^3J = 7.3 Hz), 3.51 s (2H, $=CCH_2CO$), 2.67 s (4H, $COCH_2CH_2S$), 2.66 t (2H, C^8H_2, ^3J = 7.3 Hz), 2.58 q (2H, $SC\mathbf{H}_2CH_3$, ^3J = 7.4 Hz), 2.46 q (2H, C^7H_2, ^3J = 7.3 Hz), 2.45 q (2H, $SC\mathbf{H}_2CH_3$, ^3J = 7.4 Hz), 1.27 t (3H, CH_3, ^3J = 7.4 Hz), 1.20 t (3H, CH_3, ^3J 7.4 Hz)	206.3 (CO), 141.8, 133.7 ($2C_{quat}$), 130.7, 128.5, 127.2, 126.0 (=CH and $4C_{arom}$), 45.4, 42.0 (C^2 and C^4), 31.2, 29.4, 26.1, 26.0, 25.3 (CH_2SCH_2 and $CH_2SCH_2CH_2$), 14.8, 14.7 ($2CH_3$)
X	1690 (C=O), 1620 (C=C)	7.35–7.23 m (5H, H_{arom}), 6.45 d.d (1H, 2-H, ^3J = 17.5, ^3J = 10.4 Hz), 6.07 t (1H, CH=, ^3J = 7.2 Hz), 6.30 d.d (1H, 1-H, ^3J = 17.5, ^2J = 1.3 Hz), 5.76 d.d (1H, 1-H, ^3J = 10.4, ^2J = 1.3 Hz), 3.80 s (2H, $=CCH_2CO$), 2.69 t (2H, C^8H_2, ^3J = 7.2 Hz), 2.61 q (2H, $SC\mathbf{H}_2CH_3$, ^3J = 7.4 Hz), 2.48 q (2H, C^7H_2, ^3J = 7.2 Hz), 1.28 t (3H, CH_3, ^3J = 7.4 Hz)	197.0 (CO), 142.0, 133.6 ($2C_{quat}$), 135.2, 130.5, 128.6, 128.2, 126.9, 125.8 (2CH=, CH_2=, $4C_{arom}$), 42.4 (C^4), 31.0, 29.3, 25.8 ($CH_2SCH_2CH_2$), 14.6 (CH_3)
XI	1670 (C=O), 1620 (C=C)	6.40–6.33 m (2H, 3-H, 4-H), 3.24 s (2H, $COCH_2S$), 2.46 q (2H, $SC\mathbf{H}_2CH_3$, ^3J = 7.6 Hz), 1.60–1.50 m (1H, CH, cyclopropyl), 1.19 t (3H, CH_3, ^3J = 7.6 Hz), 0.96–0.93 m (2H, CH_2, cyclopropyl), 0.64–0.62 m (2H, CH_2, cyclopropyl)	193.52 (CO), 153.90, 124.51 (2HC=), 39.13 (C^1), 25.76 ($S\mathbf{C}H_2CH_3$), 14.80, 14.03 (CH, cyclopropyl, and CH_3), 9.08 ($2CH_2$, cyclopropyl)
XII	1680 (C=O), 1600 (C=C)	6.33 br.s (1H, =CH), 3.38–3.30 m (1H, CH, cyclopropyl), 3.24 s (2H, SCH_2CO), 2.52 q (2H, $SC\mathbf{H}_2CH_3$, ^3J = 7.3 Hz), 1.95 d (3H, $CH_3C=$, ^4J = 1.2 Hz), 1.25 t (3H, CH_3, ^3J = 7.3 Hz)	194.42 (CO), 162.97 (C_{quat}), 119.47 (CH=), 42.11 (C^1), 25.75 ($S\mathbf{C}H_2CH_3$), 18.80, 14.99, 14.17 (CH_3, allyl; CH, cyclopropyl; $CH_2\mathbf{C}H_3$), 7.27 ($2CH_2$, cyclopropyl)
***E*-XIII**	1680 (C=O), 1600 (C=C)	7.35–7.11 m (5H, H_{arom}), 6.34 s (1H, =CH), 3.30 s (2H, $COCH_2S$), 3.25–3.15 m (1H, CH, cyclopropyl), 2.57 q (2H, $SC\mathbf{H}_2CH_3$, ^3J = 7.4 Hz), 1.26 t (3H, CH_3, ^3J = 7.4 Hz), 0.93–0.90 m (2H, CH_2, cyclopropyl), 0.51–0.49 m (2H, CH_2, cyclopropyl)	195.36 (CO), 163.90 (C=), 138.64, 127.87, 127.75, 127.62 ($6C_{arom}$), 124.21 (=CH), 42.21 (C^1), 25.78 ($S\mathbf{C}H_2CH_3$), 14.80, 14.03 (CH, cyclopropyl, and CH_3), 7.45 ($2CH_2$, cyclopropyl)
***Z*-XIII**	1680 (C=O), 1600 (C=C)	7.41–7.10 m (5H, H_{arom}), 6.29 s (1H, =CH), 2.93 s (2H, $COCH_2S$), 2.41 q (2H, $SC\mathbf{H}_2CH_3$, ^3J = 7.4 Hz), 1.82–1.64 m (1H, CH, cyclopropyl), 1.18 t (3H, CH_3, ^3J = 7.4 Hz), 0.89–0.84 m (2H, CH_2, cyclopropyl), 0.65–0.59 m (2H, CH_2, cyclopropyl)	194.51 (CO), 160.52 (C=), 137.76 127.99, 127.90, 127.74 ($6C_{arom}$), 122.57 (=CH), 40.53 (C^1), 25.71 ($S\mathbf{C}H_2CH_3$), 19.98, 14.09 (CH, cyclopropyl, and CH_3), 7.28 ($2CH_2$, cyclopropyl)
XIV	1700 (C=O), 3350–3580 (OH)	3.31 s (2H, $COCH_2S$), 3.29 br.s (1H, OH), 2.87 s (2H, $COCH_2C$), 2.51 q (2H, $SC\mathbf{H}_2CH_3$, ^3J = 7.4 Hz), 1.26 t (3H, CH_3, ^3J = 7.4 Hz), 0.92–0.85 m (2H, CH, cyclopropyl), 0.50–0.25 m (8H, $4CH_2$, cyclopropyl)	207.43 (CO), 70.23 (C^4), 49.83, 42.37 (C^3, C^1), 25.74 ($S\mathbf{C}H_2$-CH_3), 19.54 (2CH, cyclopropyl), 13.91 (CH_3), 0.22, –0.18 ($4CH_2$, cyclopropyl)

Table. (Contd.)

Compound no.	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm
XV	1710 (C=O), 3320–3580 (OH)	3.3 br.s (1H, OH), 2.87–2.72 m (4H, $COCH_2CH_2S$), 2.69 s (2H, $COCH_2$), 2.55 q (2H, SCH_2CH_3, ^3J = 7.4 Hz), 1.26 t (3H, CH_3, ^3J = 7.4 Hz), 0.92–0.82 m (2H, CH, cyclopropyl), 0.50–0.24 m (8H, $4CH_2$, cyclopropyl)	211.62 (CO), 70.15 (C^1), 52.24, 45.38 (C^2, C^4), 26.09, 24.72 (C^5, SCH_2CH_3), 19.53 (2CH, cyclopropyl), 14.52 (CH_3), 0.26, –0.25 ($4CH_2$, cyclopropyl)

[a] The yield and analytical data are given for isomeric mixture **VIIIa**/*E*-**VIIIb**/*Z*-**VIIIb**.
[b] Mixture of isomers.

Thus, only the reaction of complex **I** with 1-cyclopropyl-1-phenylethylene is accompanied by opening of the three-membered ring. In all other cases, complexes **I** and **II** react with cyclopropyl-substituted alkenes without opening or rearrangement of the cyclopropane ring due to fast binding of primary cationic intermediates by sulfur atom of the ethylthio group. Smooth acylation of labile system with complexes **I** and **II** opens new prospects in the synthesis of difficultly accessible cyclopropane derivatives.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Varian VXR-400 spectrometer (400 MHz) in $CDCl_3$. The ^{13}C NMR spectra were obtained on the same instrument at 100 MHz. Hexamethyldisiloxane (δ 0.06 ppm) and tetramethylsilane (δ 0.00 ppm) were used as internal reference. The IR spectra were measured on a UR-20 spectrophotometer from samples prepared as thin films. The spectral and analytical data for compounds **VII**–**XV** are given in table.

2-(Ethylthio)acetyl fluoride and 3-(ethylthio)propionyl fluoride were synthesized from the corresponding acyl chlorides [18] by distillation over KHF_2 and ZnF_2, respectively; $EtSCH_2COF$: bp 55–57°C (30 mm); $EtSCH_2CH_2COF$: bp 63–65°C (24 mm).

Acylation of cyclopropyl-substituted alkenes with complexes I and II (*general procedure***).** A solution of 0.02 mol of 2-(ethylthio)acetyl fluoride or 3-(ethylthio)propionyl fluoride in 50 ml of methylene chloride was saturated with gaseous boron trifluoride at –60°C under vigorous stirring. The mixture was stirred at that temperature for 10 min, and a solution of 0.02 mol of alkene in 30 ml of methylene chloride was added. The cooling bath was removed, and the mixture was stirred until it warmed up to room temperature. The mixture was slowly poured into 200 ml of a saturated solution of $KHCO_3$ and was stirred for 1 h. The organic phase was separated, and the aqueous phase was extracted with diethyl ether (2×50 ml). The combined extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The products were purified by column chromatography using hexane–ether (4 : 1) as eluent.

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