Electrophilic Sulfides(II) as a Novel Catalyst. VI.[1] Reaction of Sulfonium Ylides with Arenesulfenyl Thiocyanates

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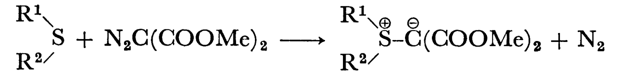
(Received July 28, 1977)

Arenesulfenyl thiocyanates (Ar-S-SCN) reacted with sulfonium ylides ($\text{MeR}\overset{\oplus}{\text{S}}\text{-}\overset{\ominus}{\text{C}}\text{(COOMe)}_2$) in chloroform at room temperature, forming sulfonium ion, $\text{MeRS}^{\oplus}\text{-C(SAr)(COOMe)}_2\ \text{SCN}^{\ominus}$, which further reacted. The mechanism of this reaction was discussed.

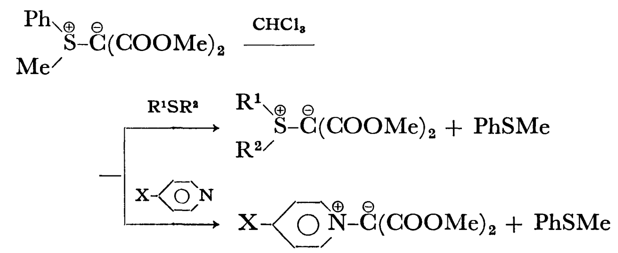
We have reported that the disulfides containing electron-withdrawing substituents, $\overset{\delta-}{\text{R}}\leftarrow\overset{\delta+}{\text{S}}\text{—}\overset{\delta+}{\text{S}}\rightarrow\overset{\delta-}{\text{R}}$ (R=OMe, CN, CF_3, and COPh), react as novel catalysts for several reactions of sulfonium ylides.[2-5] In the presence of these disulfides as catalysts, the following reactions take place smoothly at room temperature.

a) Formation of sulfonium ylides by condensation between alkyl sulfides and diazo esters:[2]



$$\text{R}^1\text{R}^2\text{S} + \text{N}_2\text{C(COOMe)}_2 \longrightarrow \text{R}^1\text{R}^2\overset{\oplus}{\text{S}}\text{-}\overset{\ominus}{\text{C}}\text{(COOMe)}_2 + \text{N}_2$$

b) Transylidation of sulfonium ylides:[3,5]



c) Olefin formation:[4]

$$2\,\text{Me}_2\overset{\oplus}{\text{S}}\text{-}\overset{\ominus}{\text{C}}\text{(COOMe)}_2 \xrightarrow{\text{CHCl}_3} \text{(MeOOC)}_2\text{C=C(COOMe)}_2 + 2\text{Me}_2\text{S}$$

$$2\,\text{Me}_2\overset{\oplus}{\text{S}}\text{-}\overset{\ominus}{\text{C}}\text{(CN)}_2 \xrightarrow{\text{CHCl}_3} \text{(NC)}_2\text{C=C(CN)}_2 + 2\text{Me}_2\text{S}$$

Under the above reaction conditions, these disulfides are not reactants, but catalysts.

Recently, we found that arenesulfenyl thiocyanates (Ar-S-SCN) react with sulfonium ylides $\text{MeR}\overset{\oplus}{\text{S}}\text{-}\overset{\ominus}{\text{C}}\text{(COOMe)}_2$. Very little has been published on the reaction of sulfonium ylides with disulfides.[6] The results are described and the mechanism of the reactions are discussed in this paper.

Results and Discussion

As is shown in Table, arenesulfenyl thiocyanates reacted with sulfonium ylides in chloroform at room temperature. In these reactions, alkanesulfenyl thiocyanates R-S-SCN (R=Et, *t*-Bu) did not react with sulfonium ylide **1a**, but arenesulfenyl thiocyanates Ar-S-SCN (Ar=Ph, p-Me-C_6H_4, and 2-$C_{10}H_7$) reacted smoothly with ylides **1a**—**e**. The above results are probably ascribable to the smaller electron density on the sulfur atoms of arenesulfenyl thiocyanates compared with that of alkanesulfenyl thiocyanates due to the presence of the electron-withdrawing aryl groups.

$$\overset{\delta-}{\text{Ar}}\leftarrow\overset{\delta+}{\text{S}}\rightarrow\overset{\delta-}{\text{SCN}} \qquad \text{R}\rightarrow\overset{\delta\delta+}{\text{S}}\rightarrow\overset{\delta-}{\text{SCN}}$$

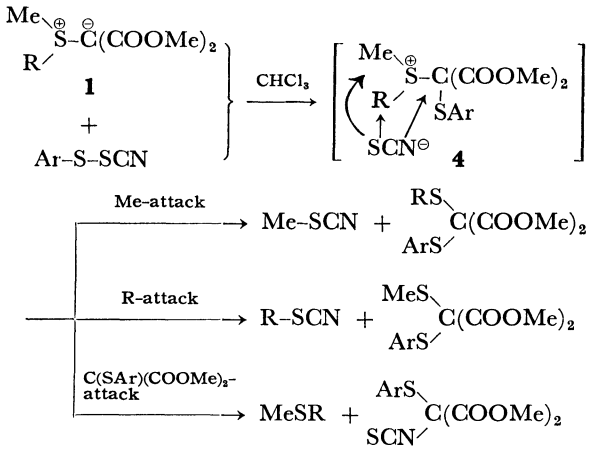
The S-S bonds of disulfides containing two different substituents are easily cleaved by nucleophilic attacks, compared to those of disulfides containing two equal substituents.[7] As is shown in Table, ylides **1a**—**e** and arenesulfenyl thiocyanates react, forming sulfonium ions and anion $SCN^{\ominus}$, which further react in three different ways (namely, Me-attack, R-attack, and C(SAr)-

Table 1. Reaction of sulfonium ylides with arenesulfenyl thiocyanates

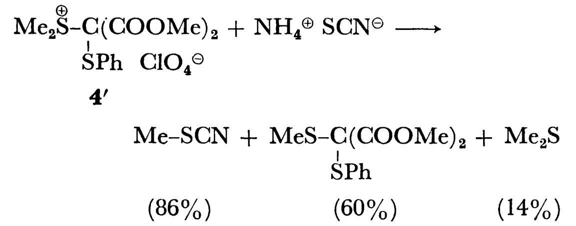
1	R	Ar	Products (mol %) Me-attack Me-SCN[a]	Me-attack RS(ArS)CQ$_2$[b,c]	R-attack R-SCN[d]	R-attack MeS(ArS)CQ$_2$[a,c]	C(SAr)Q$_2$-attack MeSR[a]	C(SAr)Q$_2$-attack ArS(SCN)CQ$_2$[c,e]
1a	Ph	Et			no reaction			
1a	Ph	*t*-Bu			no reaction			
1a	Ph	Ph	0	0	—	—	84	58
1b	Me	Ph	78	74	—	—	14	(14)
1b	Me	*p*-Me-C_6H_4	80	73	—	—	13	(13)
1b	Me	2-$C_{10}H_7$	76	75	—	—	21	(21)
1c	Et	Ph	50±3	(50±3)	(30±3)	30±3	19±2	(19±2)
1d	*i*-Pr	Ph	20±2	(20±2)	(40±2)	40±2	40±2	(40±2)
1e	PhCH$_2$	Ph	9±2	(9±2)	90±2	90±2	0	0

a) Determined from its methyl singlet absorption. b) The amount of RS(ArS)CQ$_2$ was estimated by assuming the equimolar formation of Me-SCN and RS(ArS)CQ$_2$. c) Q=COOMe. d) The amount of $PhCH_2$-SCN was determined from its singlet δ=4.11 ppm. The amounts of other R-SCN's were estimated from the assumption of the equimolar formation of R-SCN and MeS(ArS)CQ$_2$ (determined from its MeS singlet). e) The amount of ArS(SCN)CQ$_2$ was estimated by assuming the equimolar formation of MeSR and ArS(SCN)CQ$_2$.

$(COOMe)_2$-attack).



Usually **1** and arenesulfenyl thiocyanates were allowed to react without isolating intermediates **4**. However, when **4′** shown below was separately prepared and allowed to react with ammonium thiocyanate, the results obtained were consistent with those shown in Table.



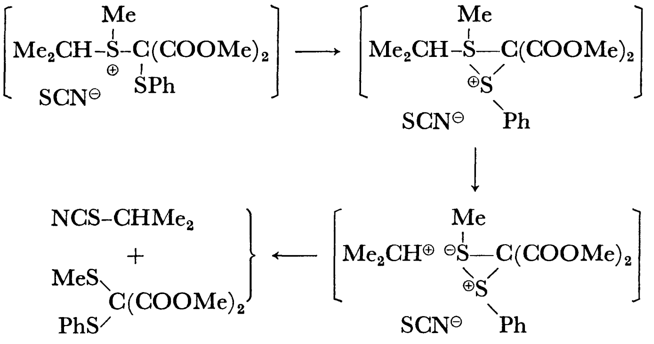
$$\underset{\substack{\text{SPh}\ \ ClO_4^{\ominus}\\ \mathbf{4'}}}{Me_2\overset{\oplus}{S}\text{-}C(COOMe)_2} + NH_4^{\oplus}\,SCN^{\ominus} \longrightarrow$$

$$\underset{(86\%)}{Me\text{-}SCN} + \underset{(60\%)}{MeS\text{-}\underset{SPh}{C}(COOMe)_2} + \underset{(14\%)}{Me_2S}$$

When R in **4** is an alkyl group, competitive S_N2 attacks on the methyl and alkyl groups are expected. The relative reactivities of alkyl groups on sulfonium ions with anion $SCN^{\ominus}$ (the ratios between the yields of methylated and alkylated products) are $PhCH_2$ 10.0, *i*-Pr 2.0, Me 1.0, and Et 0.60. These results suggest that these reactions involve an S_N1-like process. The order of the reactivity of alkyl groups for the reaction between $MeR\overset{\oplus}{S}$-C(SPh)$(COOMe)_2$ and anion $Cl^{\ominus}$ is:[8]

$PhCH_2$ (∞) > *i*-Pr (4.2) > Me (1.0) > Et (0.85)

Therefore, the R-attack course of the reactions of **4** is probably expressed as follows.[8]



Experimental

Materials. Sulfonium bis(methoxycarbonyl)methylides **1a**—**e** were prepared by copper sulfate-catalyzed decomposition of dimethyl diazomalonate in large excess sulfides[9] and by transylidation.[3,5] Ethanesulfenyl thiocyanate (bp 40—45 °C/8 mmHg), 2-methyl-2-propanesulfenyl thiocyanate, benzenesulfenyl thiocyanate, *p*-toluenesulfenyl thiocyanate and 2-naphthalenesulfenyl thiocyanate (mp 62.5—63 °C (lit, 61.5—63 °C)) were synthesized by the methods described in the literature.[10] Sulfonium salt **4′** was prepared by the dropwise addition of a CCl_4 solution of benzenesulfenyl chloride (1.45 g) to a nitromethane solution of **1a** (1.94 g) and silver perchlorate (2.07 g) at 0 °C. Yield, 3.6 g (90%); recrystallized from ethanol; mp 105—106 °C; IR (KBr), 1740 cm^{-1} (ν_{CO}); NMR (DMSO-d_6), δ=7.60 (5H, s, PhS), 3.93 (6H, s, COOMe) and 3.20 (6H, s, $Me\overset{\oplus}{S}$). Found: C, 38.76; H, 4.25. Calcd for $C_{13}H_{17}O_8ClS_2$: C, 38.96; H, 4.27.

*Reactions of Ylide **1a** with Alkanesulfenyl Thiocyanates.* a) A $CDCl_3$ solution of **1a** (0.57 mmol) and ethanesulfenyl thiocyanate (0.78 mmol) did not react. After 1 day, ylide **1a** (80%) was recovered. b) A $CDCl_3$ solution of **1a** (0.80 mmol) and 2-methyl-2-propanesulfenyl thiocyanate (0.82 mmol) did not react under the same condition. After 1 day, ylide **1a** (80%) was recovered.

*Reactions of Ylides **1a** and **1b** with Arenesulfenyl Thiocyanates.* a) A chloroform (13 g) solution of **1b** (2.08 g, 10.9 mmol) was mixed with PhS–SCN (2.0 g, 11.9 mmol) at room temperature. After 30 min, the ylide carbonyl absorption (1630 and 1670 cm^{-1}) were replaced by the ester absorption (1730 cm^{-1}). The NMR spectra of the reaction mixture showed the presence of MeSCN (δ=2.56, s; 78%), Me_2S (2.01, s; 14%) and MeS(PhS)C$(COOMe)_2$ (2.15, s, MeS; 74%). The low-boiling fractions from the mixture were trapped in liquid nitrogen, and the presence of MeSCN was shown by NMR (δ=2.59, s) and IR (ν_{SCN} 2150 cm^{-1}, strong and sharp) spectroscopy. The high-boiling fractions were chromatographed (Florisil), and the white crystals obtained from the benzene eluates were found to be MeS(PhS)C$(COOMe)_2$ (2.30 g, 8.07 mmol; 74%); mp 71—72 °C; IR (KBr), 1730 cm^{-1} (ν_{CO}); NMR (CCl_4), δ=2.15 (3H, s, MeS), 3.64 (6H, s, COOMe) and 7.30 (5H, s, PhS). Found: C, 50.52; H, 4.93%. Calcd for $C_{12}H_{14}O_4S_2$: C, 50.33; H, 4.93%. b) In a similar manner, a mixture of **1b** (3.10 g, 16.2 mmol) and *p*-Me-C_6H_4-S-SCN (3.0 g, 16.6 mmol) in chloroform (23 g) gave MeSCN (δ=2.55, s; 80%), Me_2S (2.10, s; 13%) and MeS (*p*-Me-C_6H_4S)-C$(COOMe)_2$ (from benzene eluates; 3.54 g, 11.8 mmol; 73%); mp 60—61 °C; IR (KBr), 1740 cm^{-1} (ν_{CO}); NMR (CCl_4), δ=2.15 (3H, s, MeS), 2.33 (3H, s, *p*-Me), 3.67 (6H, s, COOMe) and 7.18 (4H, q, C_6H_4). Found: C, 51.85; H, 5.33%. Calcd for $C_{13}H_{16}O_4S_2$: C, 52.00; H, 5.37%. c) A mixture of a $CHCl_3$ (27 g) solution of **1b** (1.00 g, 5.21 mmol) and 2-$C_{10}H_7$S-SCN (1.09 g, 5.64 mmol) gave MeSCN (δ=2.51, s; 76%), Me_2S (2.09, s; 21%) and MeS (2-$C_{10}H_7$S)-C$(COOMe)_2$ (from benzene eluates; 1.33 g, 3.96 mmol; 75%); mp 84—85 °C; IR (KBr), 1740 cm^{-1} (ν_{CO}); NMR ($CDCl_3$), δ=2.27 (3H, s, MeS), 3.73 (6H, s, COOMe) and 7.20—8.05 (7H, m, 2-$C_{10}H_7$). Found: C, 57.00; H, 4.82%. Calcd for $C_{16}H_{16}O_4S_2$: C, 57.14; H, 4.80. d) In a similar manner, a mixture of **1a** (1.75 g, 6.87 mmol) and PhS–SCN (1.17 g, 7.0 mmol) in chloroform (9 g) gave MeSPh (from hexane eluates; 0.71 g, 5.75 mmol; 84%) and PhS(S=C=N–)-C$(COOMe)_2$ (oil from benzene eluates; 1.19 g, 4.0 mmol; 58%; IR (neat), 1740 cm^{-1} (ν_{CO}) and 2100 cm^{-1} ($\nu_{N=C=S}$, strong and broad);[11] NMR (CCl_4), δ=3.75 (6H, s, COOMe) and 7.16—7.55 (5H, m, PhS)).

*Reaction of Sulfonium Ion **4′** with Thiocyanate Ion.* A DMSO-d_6 solution of **4′** (1.0 mmol) and ammonium thiocyanate (2.0 mmol) was heated at 50 °C for 5 min. The NMR spectrum of the reaction mixture showed the presence of MeSCN (δ=2.67, s; 86%), MeS(PhS)C$(COOMe)_2$ (2.20, s, MeS; 60%) and Me_2S (2.07, s; 14%).

*Reactions of Ylides **1c**—**e** with Benzenesulfenyl Thiocyanate.* The $CDCl_3$ solution of ylides **1c**—**e** (0.7—1.0 mmol) and PhS-SCN (0.8—1.1 mmol) containing nitromethane (internal standard, 50 µl, 0.79 mmol) were allowed to react in NMR tubes at 25 °C, and the amounts of the reaction products were determined from their singlet methyl absorption by NMR spectroscopy (see Table); $\underline{\text{Me}}$-SCN (δ=2.56), $\underline{\text{Me}}_2\text{S}$ (2.0—2.10), $\underline{\text{Me}}$SEt (2.05—2.12), $\underline{\text{Me}}$SPr-*i* (2.10) and $\underline{\text{Me}}$S(PhS)-$C(COOMe)_2$ (2.19—2.20).

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