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Trapping of in situ Prepared Arylsulfenyl Isocyanates with Alcohols and Amines. Preparation of Arylsulfenylcarbamates and Arylsulfenylureas[1)]

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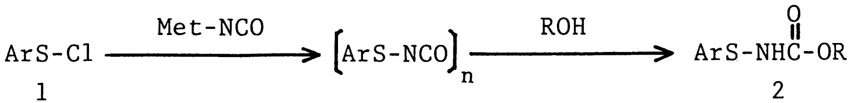
Arylsulfenyl isocyanates, which were in situ prepared from arylsulfenyl chlorides and silver (or sodium) cyanate, reacted with alcohols and primary amines at carbon of the isocyanato group to afford the corresponding arylsulfenylcarbamates and arylsulfenylureas, respectively.

Compared with sulfonyl and sulfinyl isocyanates (RSO_2-NCO and RSO-NCO), there are a few experimental studies on sulfenyl isocyanates (RS-NCO). That is due to the less stability of divalent sulfur isocyanates than other higher valent ones. Since 1963, beginning with the work of Emeleus and Hass,[2)] some reports on isolation and reaction of alkylsulfenyl isocyanates[3)] have appeared, whereas there has been no report on arylsulfenyl isocyanates only except for pentafluorobenzenesulfenyl isocyanate.[4)]

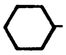
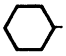
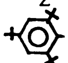
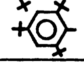
During our studies on isocyanic acid and its derivatives, we have a great interest in the chemical properties of these divalent arylsulfenyl isocyanates. We wish to describe here the trapping of in situ prepared arylsulfenyl isocyanates with alcohols and amines.

Phenyl- and 2,4,6-tri-t-butylphenylsulfenyl chlorides were in situ prepared by treatment of the corresponding disulfides with sulfuryl chloride in dichloromethane and used without further purification. 2-Nitro- and 2,4-dinitrophenylsulfenyl chlorides were used after recrystallization. These arylsulfenyl chlorides were allowed to react with metal cyanate (NaNCO/CH_3CN or AgNCO/benzene). Attempts to isolate resulting arylsulfenyl isocyanates by distillation or crystallization were not successful. The IR data of the reaction mixture (benzene and $CHCl_3$) showed existence of carbonyl groups (1690-1790 cm^{-1}) but the absorption of isocyanato groups could not be detected except for the case of 2,4,6-tri-t-butylphenylsulfenyl isocyanate. These data suggested that the other isocyanates existed as a polymeric or oligomeric form like pentafluorobenzenesulfenyl isocyanate[4)] even in the reaction mixture. In case of 2,4,6-tri-t-butylphenylsulfenyl isocyanate, an additional peak was observed at 1940 cm^{-1}, which may be due to a S-N=C=O group. The in situ prepared arylsulfenyl isocyanates were treated with alcohols and primary amines. In the cases except for that of 2,4-dinitrophenylsulfenyl isocyanate, the corresponding arylsulfenylcarbamates and arylsulfenylureas were obtained as stable compounds (Tables 1 and 2). Reaction of 2,4-dinitrophenylsulfenyl isocyanate with alcohols and amines afforded the corresponding sulfenates and sulfenamide as a major

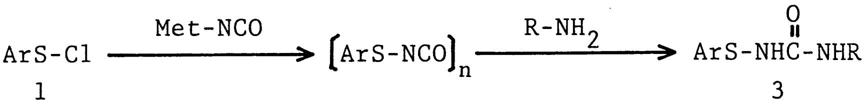


$$\underset{1}{ArS\text{-}Cl} \xrightarrow{Met\text{-}NCO} [ArS\text{-}NCO]_n \xrightarrow{ROH} \underset{2}{ArS\text{-}NH\overset{O}{\overset{\|}{C}}\text{-}OR}$$

Table 1. Preparation of Alkyl Arylsulfenylcarbamates 2

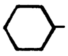
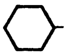
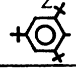
Run	Ar of 1	Met-NCO	R-OH	2	Yield/%$^{a)}$	Mp/°C
a	Ph	AgNCO	Me-OH	2a	47	44.0-45.0
b	Ph	AgNCO	$PhCH_2$-OH	2b	23	78.0-79.0
c	Ph	AgNCO	-OH	2c	48	60.0-61.0
d	$2\text{-}NO_2PH$	NaNCO	-OH	2d	10	144.0-145.0
e		AgNCO	Me-OH	2e	69	semisolid
f		AgNCO	$PhCH_2$-OH	2f	42	oil

a) Isolated yields, not optimized. All the new compounds have the reasonable ^1H NMR, IR, or elemental analysis data.



$$\underset{1}{ArS\text{-}Cl} \xrightarrow{Met\text{-}NCO} [ArS\text{-}NCO]_n \xrightarrow{R\text{-}NH_2} \underset{3}{ArS\text{-}NH\overset{O}{\overset{\|}{C}}\text{-}NHR}$$

Table 2. Preparation of N-Alkyl-(or Aryl-)N'-Arylsulfenylureas 3

Run	Ar of 1	Met-NCO	$R\text{-}NH_2$	3	Yield/%$^{a)}$	Mp/°C
a	Ph	AgNCO	$Ph\text{-}NH_2$	3a	36	149.0-150.5
b	Ph	AgNCO	$PhCH_2\text{-}NH_2$	3b	52	157.0-157.5
c	Ph	AgNCO	-NH_2	3c	50	167.5-168.5
d	Ph	AgNCO	$^iPr\text{-}NH_2$	3d	52	149.0-149.5
e	$2\text{-}NO_2Ph$	NaNCO	$Ph\text{-}NH_2$	3e	42	224.0
f	$2\text{-}NO_2Ph$	NaNCO	-NH_2	3f	21	215.0-219.0
g		AgNCO	$^iPr\text{-}NH_2$	3g	54	168.0-169.0

a) Isolated yields, not optimized. All the new compounds have the reasonable ^1H NMR, IR, or elemental analysis data.

product similar to that of pentafluorobenzenesulfenyl isocyanate$^{4)}$ in 10-30% yields. Electron-withdrawing aryl groups tended to destabilize the strength of the S-NH-C(O) group or accelerate nucleophilic attack on sulfur atom of the S-N=C=O group. A further study is underway.

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References

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