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THE TRANSYLIDATION REACTION OF A SELENONIUM YLIDE WITH SULFIDES

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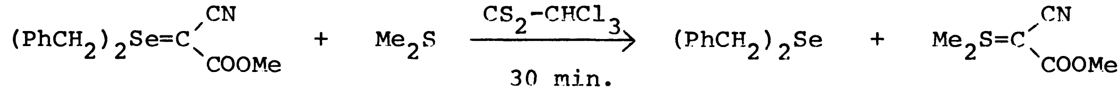
Several dialkylsulfonium ylides were obtained almost quantitatively by the transylidation reaction of dibenzylselenonium cyano(methoxycarbonyl)methylide with alkyl sulfides in the presence of CS_2.

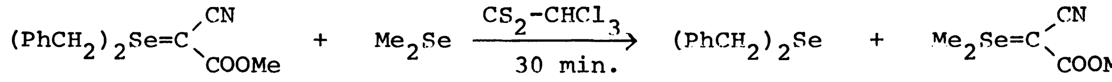
A variety of stabilized sulfonium ylides have been synthesized by photolysis of diazo-compounds in sulfides.[1] The dehydration between alkyl sulfoxides and active methylene compounds in the presence of dehydrating agents is an alternative synthetic method for some aliphatic sulfonium ylides.[2]

In this communication we report the results of a new ylide-exchange reaction giving a number of alkylsulfonium ylides.[3] Dibenzylselenonium cyano(methoxycarbonyl)-methylide(1 mmol), which was quite conveniently obtainable from dibenzyl selenoxide and the corresponding methylene compound,[4] was allowed to react with 10-fold excess of dimethyl sulfide in 20 ml of a CS_2-$CHCl_3$(1:1 V/V) mixture at room temperature for 30 minutes. Evaporation of the solvents and then extraction of dibenzyl selenide so formed with hexane afforded a quantitative yield of dimethylsulfonium cyano(methoxycarbonyl)methylide as a solid residue.



$$(\mathrm{PhCH_2})_2\mathrm{Se{=}C}\begin{matrix}\mathrm{CN}\\ \mathrm{COOMe}\end{matrix} + \mathrm{Me_2S} \xrightarrow[30\ \mathrm{min.}]{\mathrm{CS_2{-}CHCl_3}} (\mathrm{PhCH_2})_2\mathrm{Se} + \mathrm{Me_2S{=}C}\begin{matrix}\mathrm{CN}\\ \mathrm{COOMe}\end{matrix}$$

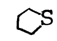
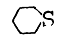
A similar transylidation took place very smoothly with some other acyclic and cyclic sulfides, and the yields of sulfonium ylides were quite satisfactory except sterically hindered di-t-butyl sulfide. Meanwhile, dimethyl selenide, instead of dimethyl sulfide, produced the expected selenonium ylide as well within 30 minutes of reaction time.



$$(\mathrm{PhCH_2})_2\mathrm{Se{=}C}\begin{matrix}\mathrm{CN}\\ \mathrm{COOMe}\end{matrix} + \mathrm{Me_2Se} \xrightarrow[30\ \mathrm{min.}]{\mathrm{CS_2{-}CHCl_3}} (\mathrm{PhCH_2})_2\mathrm{Se} + \mathrm{Me_2Se{=}C}\begin{matrix}\mathrm{CN}\\ \mathrm{COOMe}\end{matrix}$$

The results thus obtained are summarized in Table 1.

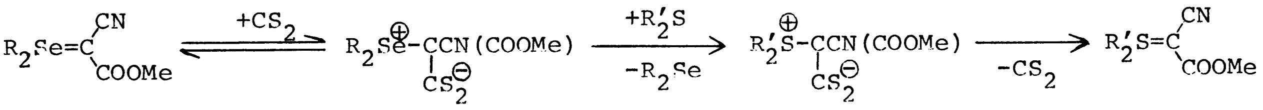
Table 1. The Reaction of Dibenzylselenonium cyano(methoxycarbonyl)methylide(I) with Sulfides(II) in CS_2-$CHCl_3$ at Room Temperature

Sulfide (II)	Mole ratio, (II)/(I)	Reaction time, hr	Products			
			Selenide	Sulfonium ylide[a)]		
			Yield,%	Yield,%	Mp, °C	nmr, ppm from internal TMS
Me_2S	10	0.5	99	98	158-160	3.66(s) 2.80(s)
Me_2Se	5	0.5	99	66[b)]	149-151	3.69(s) 2.70(s)
Et_2S	10	18	88	94	96 -97	3.70(s) 2.8-3.4(m) 1.4(t)
t-BuSMe	10	3	72	77[c)]	97 -98	3.70(s) 2.7(s) 1.45(s)
	10	24	98	trace[d)]		
	10	1	98	95	89.5-90.5	3.68(s) 3.2-3.5(m) 1.9-2.5(m)
	5	3	86	90	85 -87	3.70(s) 2.8-3.4(m) 2.0-2.3(m) 1.6-1.8(m)
	5	3	77	84	99 -101	3.75(s) 3.1-3.6(m) 1.6-1.9(m) 2.0-2.4(m)

a) Satisfactory analytical data were obtained for all the compounds. b) Dimethyl-selenonium cyano(methoxycarbonyl)methylide. c) 10% of dimethyl dicyanofumarate was obtained. d) Not isolated due to its low yield, but the presence was confirmed by the ir spectrum of the reaction mixture; 2170(s,C≡N), 1680(s,C=O) cm^{-1}.

However, the sulfonium ylides of strained thiirane and thietane could not be obtained because of the low nucleophilicity of their sulfur atom; actually, the reaction of the former sulfide gave dimethyl dicyanofumarate rather than the sulfonium ylide, as already reported in the previous paper.[5)]

The transylidation described here does not occur without the addition of carbon disulfide, strongly suggesting that the reaction proceeds through an initial CS_2-addition on the carbon of selenonium ylide followed by replacement of the selenide moiety with sulfides eventually giving the sulfonium ylides, as shown below. The driving force is apparently the formation of the S=C bond far stronger than the Se=C bond.



$$R_2Se{=}C\begin{smallmatrix}CN\\COOMe\end{smallmatrix} \overset{+CS_2}{\rightleftarrows} R_2\overset{\oplus}{Se}-\underset{CS_2^{\ominus}}{\underset{|}{C}}CN(COOMe) \xrightarrow[-R_2Se]{+R'_2S} R'_2\overset{\oplus}{S}-\underset{CS_2^{\ominus}}{\underset{|}{C}}CN(COOMe) \xrightarrow[-CS_2]{} R'_2S{=}C\begin{smallmatrix}CN\\COOMe\end{smallmatrix}$$

References

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