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A REACTION OF SELENONIUM YLIDES WITH EPISULFIDES

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Dialkylselenonium cyano(methoxycarbonyl)methylides reacted catalytically in $CHCl_3$ at room temperature with aliphatic episulfides to give mainly the reduced selenides and dicyanofumarate.

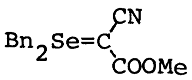
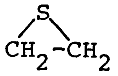
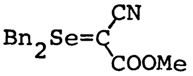
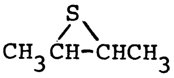
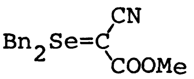
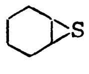
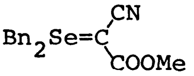
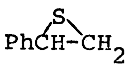
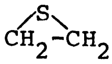
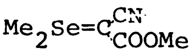
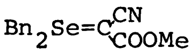
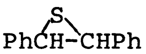
We recently described a catalytic decomposition of dibenzylselenonium disubstituted methylides by thioureas, thioamides, and CS_2 affording dibenzylselenide and tetrasubstituted olefins, in which an episulfide was postulated as a transient intermediate.1)

In connection with our interests in reductions of the same ylides,2) we have examined the reaction of these ylides with episulfides and have found that some episulfides also are quite effective in catalytic decomposition of selenonium ylides.

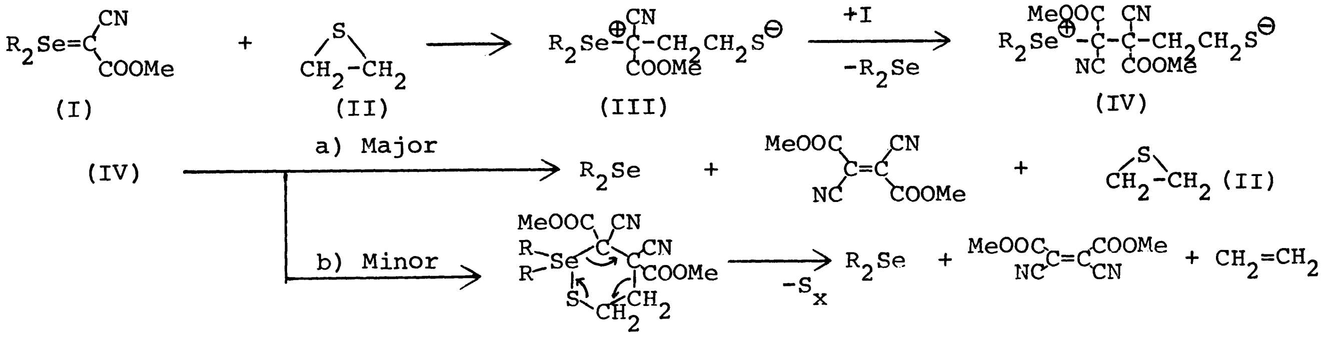
When one mmole of dibenzylselenonium cyano(methoxycarbonyl)methylide in 10 ml of $CHCl_3$ was allowed to react with one molar equivalent of ethylene episulfide at room temperature for 10 min, a crystalline product, dicyanofumarate, precipitated and evaporation of the solvent followed by thin-layer chromatography of the resulting residue gave dibenzyl selenide and elemental sulfur in quantitative and low yields, respectively. The nmr spectrum of the reaction mixture showed that ethylene derived from the episulfide is produced in less than 10% yield.3) In distinct contrast to the reaction with thioamides,1) any significant effect of mole ratio of episulfide to the ylide ranging from 0.2 to 5 upon product yields and distribution was not observed, clearly suggesting that episulfide could well act as a fairly effective catalyst for decomposition of the ylides. Other episulfides of cyclohexene, styrene, and 2-butene could also be utilized for this decomposition. The results thus obtained are summarized in Table 1. Meanwhile, with 1,2-diphenylethylene episulfide no reaction took place probably due to steric hindrance toward nucleophilic attack of the ylide on one of the episulfide carbon atoms.

Thus, a mechanism involving the first formation of an adduct(III) followed by fragmentation[4] of the secondary formed intermediate(IV), as depicted below, would be the most plausible one, where the episulfide is regenerated and successively used according to path a.

Table 1. The reaction of a few selenonium ylides

Selenonium Ylide(I)[f]	Episulfide (II)	Mole Ratio (II)/(I)	Products, isolated %[a]			Recovered Episulfide
			Selenide	Dicyano-fumarate	Olefin	
 $Bn_2Se=C(CN)COOMe$		10	(100)	(86)	$CH_2=CH_2$[b]	
		1	92(100)	68(88)	$CH_2=CH_2$[b]	(85)[d]
		0.1	(100)	(84)	$CH_2=CH_2$[b]	(67)[d]
 $Bn_2Se=C(CN)COOMe$		1	86	62		
 $Bn_2Se=C(CN)COOMe$		5	(100)	(86)	C_6H_4(20)[c]	
		1	89(100)	73(85)	C_6H_4(20)[c]	
		0.3	95(100)	70(80)	C_6H_4(16)[c]	
		0.1	91(100)	78(82)	C_6H_4(5)[c]	
 $Bn_2Se=C(CN)COOMe$		1	95	89		
		0.1	97	73		
 $Se=C(CN)COOMe$		1	e)	84	$CH_2=CH_2$[b]	
 $Me_2Se=C(CN)COOMe$		1	e)	83		
 $Bn_2Se=C(CN)COOMe$		1	no reaction			

a) Yields determined by nmr spectroscopy are denoted in parentheses. b) In trace amounts. c) Yield % relative to dibenzyl selenide produced. d) Recovered % relative to the initially used amount of ethylene episulfide. e) Yields were not determined. f) Bn stands for $PhCH_2$ group.



REFERENCES and NOTES

1) S. Tamagaki and I. Hatanaka, Chem. Lett., 1303(1976).
2) S. Tamagaki and I. Hatanaka, ibid., 301(1976).
3) The nmr peaks due to the CH_2 protons in ethylene appeared at 5.39 ppm (singlet).
4) J.B. Hendrickson, D.J. Cram, and G.S. Hammond,"Organic Chemestry," 3rd ed., McGraw-Hill, Kogakusha LTD., Tokyo, PP.600(1970).

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