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The Reaction of Dibenzylselenonium Ylides with Various Acids[1)]

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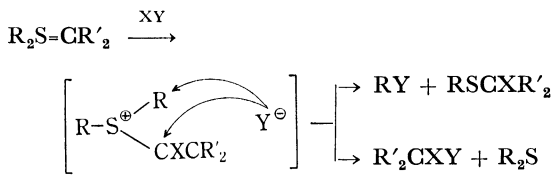
Synopsis. Dibenzylselenonium cyano(methoxycarbonyl)methylide and dibenzylselenonium dicyanomethylide react readily with strong acids at room temperature, giving 1,3-diselena compounds and active methylene compounds.

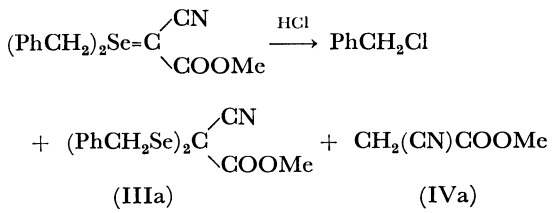
The reactions of stable alkylsulfonium ylides with electrophilic reagents such as acids,[2)] molecular halogens,[3)] and acyl peroxides[4)] have been intensively studied and the reactions are assumed to proceed by a common mechanism in which sulfonium intermediates are first formed, as follows.



However, no report seems to have been presented so far for the decomposition of selenonium ylides by electrophilic reagents. We have examined the reaction of dibenzylselenonium ylides with various acids, and found that the reaction involves an α-carbon attack by the counter anions in the initial stage,[5)] similar to the reactions mentioned above, one of the products, however, eventually giving disproportionation products, *i.e.*, 1,3-diselena compounds and active methylene compounds.

Results and Discussion

Dibenzylselenonium cyano(methoxycarbonyl)methylide (Ia) was allowed to react with dried gaseous hydrogen chloride and the equivalent of trifluoroacetic acid in chloroform or with an equimolar amount of aqueous sulfuric and nitric acids in acetonitrile at room temperature. The reaction with hydrogen chloride was followed by thin-layer chromatography. After completion of the reaction, evaporation of the solvent and the subsequent preparative thin-layer chromatographic separation of the residue gave an oily material, the structure of which was identified by its MS, IR, and NMR spectra and elemental analysis as methyl α,α-bis(benzylseleno)-α-cyanoacetate (IIIa). From another part of the TLC plate, the corresponding methylene compound (IVa) was isolated in a good yield. The products and yields are summarized in Table 1.



The NMR and IR spectra of the reaction mixture show that the appearance of some peaks is due to a substance (IIa) not isolable in the pure state and also to benzyl chloride; the former displays the IR band at 2250 and 1759 cm^{-1} due to its cyano and ester carbonyl groups and NMR peaks at 7.3 (Ph), 4.2 (CH_2), 4.03 (CH), 3.75 (OCH_3) ppm with the intensity ratio of 5 : 2 : 1 : 3, respectively; the methylene protons of the latter lie at 4.53 ppm. A similar phenomenon was observed in the reaction with other acids such as tri-

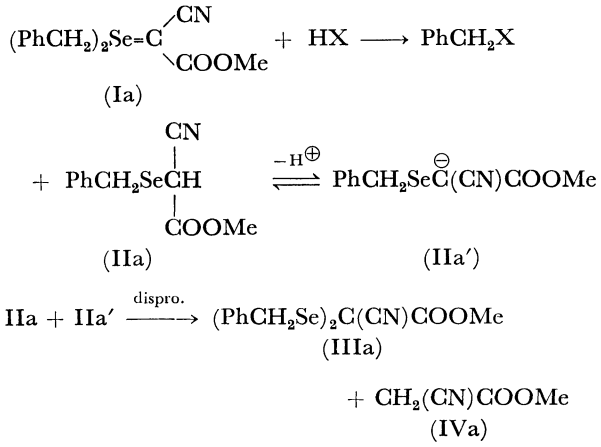
Table 1. Reaction of dibenzylselenonium ylides (I)[a)] with various acids at room temperature

$R_2SeCCNY$, Y	Solvent	Time	HX, X	Mole ratio, HX/I	Products, mol% yield		
					RX	$(RSe)_2CCNY$[b)] or others	CH_2CNY
COOMe	$CHCl_3$	10 min	Cl	c)	(100)	21	40
COOMe	$CHCl_3$	3 h	CF_3COO	1	(100)	33	d)
COOMe	CH_3CN	2 h	HSO_4	1	d)	35	d)
COOMe	CH_3CN	24 h	NO_3	1	(94)	19	31
COOMe	CH_3CN	24 h	HSO_4	10[e)]	d)	$(RSe)_2$, 31	d)
COOMe	CH_3CN	30 min	Br	2	57	$(RSe)_2$, 13 Se, 39	
CN	$CHCl_3$	2 h	CF_3COO	3	(90)	29[f)]	(20)[g)]
CN	$CHCl_3$	22 h	$CHCl_2COO$	3	(80)	$(RSe)_2$, 20	d)
CN	CH_3CN	22 h	NO_3	1	17	RSeCN, 22	d)

a) $R_2Se=C(CN)Y$: $R=PhCH_2$. b) All the compounds shown were isolated by thin-layer chromatography. c) In a solution saturated with gaseous HCl. d) Yields were not determined. e) Concentrated acid was used. f) In addition, dibenzyl diselenide was obtained in 5% yield. g) Characterization was performed by NMR. Yields determined by NMR are given in parentheses.

fluoroacetic, sulfuric, and nitric acids.

These observations demonstrate that compound (IIa) initially produced is methyl α-(benzylseleno)-α-cyanoacetate which is very stable under acidic conditions but decomposes readily, on a TLC plate, *via* disproportionation to give isolable products. Thus, the following reaction pathway is the most probable.



As was the case for Ia, dibenzylselenonium dicyanomethylide (Ib), when subjected to reaction with trifluoroacetic acid, gave benzyl trifluoroacetate almost quantitatively together with, the expected selenide, α-(benzylseleno)malononitrile (IIb) as evidenced by the NMR analysis. However, malononitrile and α,α-bis-(benzylseleno)malononitrile (IIIb) were the products isolated.

The latter was unstable and spontaneously decomposed, at room temperature within 2 days, into dibenzyl diselenide in a moderate yield. The reaction of the ylide, Ib, with hydrochloric, sulfuric, and nitric acids is complicated.

Experimental

Typical experimental procedures are as follows:

Reaction of Ia with Trifluoroacetic Acid. A mixture of Ia (1 mmol) and trifluoroacetic acid (1 mmol) was stirred in 20 ml of chloroform at room temperature for 3 h. Evaporation of the solvent and subsequent thin layer chromatography of the residue afforded an oily IIIa. The yields are given in Table 1. The NMR data (IIIa in $CDCl_3$, δ) are as follows: 7.25(10H), 4.25(4H), 3.60(3H) ppm; IR (KBr): 2230 and 1740 cm^{-1}; MS: *m/e* 439 (M^+), 342, 269, 262, 171, and 91; Found: C, 49.48; H, 3.84; N, 2.98 %. Calcd for $C_{18}H_{17}O_2NSe_2$: C, 49.72; H, 4.02; N, 3.11%.

The Reaction of Ib with Trifluoroacetic Acid. Ib (1 mmol) was suspended in a chloroform solution of trifluoroacetic acid (3 mmol). After 2 h, the reaction mixture was concentrated *in vacuo*. Preparative TLC (Kieselgel G, chloroform) afforded an oily IIIb (29%). NMR 7.25 (10H), 4.43(4H) ppm; IR(KBr): 2240 cm^{-1}; MS: *m/e* 406(M^+), 342, 262, 171 and 91; Found: C, 50.79; H, 3.71; N, 7.12%. Calcd for $C_{17}H_{14}N_2Se_2$: C, 50.51; H, 3.50; N, 6.93%.

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