CHEMISTRY LETTERS, pp. 1303-1306, 1976. Published by the Chemical Society of Japan

CATALYTIC DECOMPOSITION OF A DIBENZYLSELENONIUM YLIDE WITH THIOAMIDES

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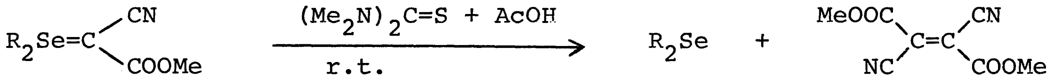
Dibenzylselenonium cyano(methoxycarbonyl)methylide was readily decomposed by the action of catalytic amounts of thioamides affording the corresponding selenide and tetra-substituted ethylene, while with increasing amounts of the thioamides the ylide was found to react in a different fashion.

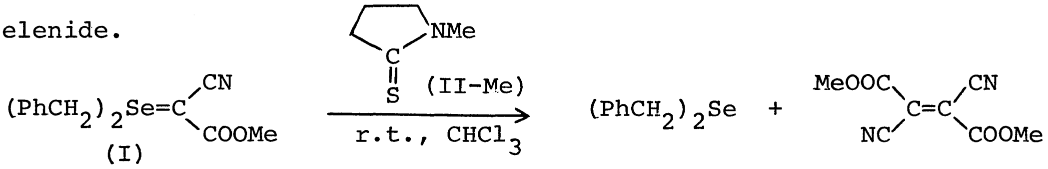
The selenium compounds such as selenonium ylides and selenoxides have been as extensively studied as those of their sulfur analogs although they exhibit some novel features. It is well known that selenoxides are much more susceptible to reductions than the sulfur counterparts.[1)] However, little work has been reported on the reduction of selenonium ylides and, up to date, a few reduction reactions accompanying olefin formation have been observed in both sulfur[2)] and selenium ylides.[3)] One of these involves the catalytic decomposition accompanying olefin formation from the ylidene portion of ylides.



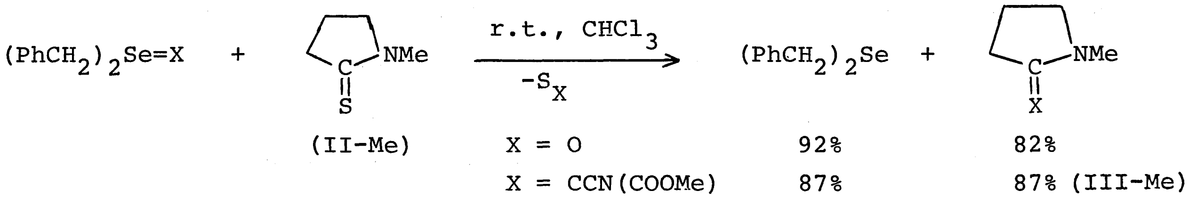
$$R_2Se{=}C(CN)(COOMe) \xrightarrow[\text{r.t.}]{(Me_2N)_2C{=}S\ +\ AcOH} R_2Se \ + \ (MeOOC)(NC)C{=}C(CN)(COOMe)$$

As a part of our continuing interest in the reduction of selenonium ylides, we now wish to report a study of the reaction of a selenonium ylide with thiono group-containing compounds, which is another example of facile catalytic decomposition of a stable ylide producing the selenide and olefin. On the other hand, we find that the reaction exhibits a marked change in products, depending on varying amounts of thioamides employed. To our knowledge, little has been known about such reaction types in ylide chemistry.

When one mmole of dibenzylselenonium cyano(methoxycarbonyl)methylide(I) was allowed to react with only 0.1 equivalent of N-methylpyrrolidine-2-thione(II-Me) in 20 ml of $CHCl_3$ at room temperature for 10 min, dimethyl dicyanofumarate[4)] was precipitated. The filtrate was concentrated by a rotary evaporator and the resultant residue was fractionated by preparative TLC with $CHCl_3$ as eluant, giving dibenzyl selenide.



However, the yields of the olefin were found to substantially decrease as the mole ratios of thioamides to the ylide were increased (Table 1). Thus, a $CHCl_3$ solution of an equimolar mixture of the ylide and a thioamide(II-Me) at room temperature gave the reduced selenide and 2-(cyanomethoxycarbonylmethylidene)-N-methylpyrrolidine (III-Me)[5)] together with precipitation of elemental sulfur. In a somewhat related reaction, the corresponding selenoxide reacted with the thioamide to yield the selenide and the corresponding amide with elimination of elemental sulfur in good yields. A similar pattern of reactions accompanying sulfur extrusion has been known so far in the reaction of DMSO with phosphine sulfide[6)] or thiophosphoric acid,[7)] and sulfilimine with carbon disulfide.[8)]



The products thus obtained were identified by elemental analyses, spectral data, and, if necessary, comparison with authentic materials. The results are summarized in Table 1.

A reaction sequence, as illustrated in Scheme 1 involving the fast formation of a thiirane intermediate(IV), is one possible mechanism; if the ylide is present always in excess to thioamide during the course of the reaction, the electronegative carbon of the intermediate(IV) would be further attacked by the still remaining ylide, eventually producing the olefin, and thus the starting thioamide is regenerated for successive use (Path a). On the other hand, in the case where the initial thioamide concentrations are kept high or equal to those of the ylide throughout the process, most of the ylide is rapidly consumed to form the intermediate, which would then collapse to lead to sulfur extrusion (Path b).

Likewise, carbon disulfide and 1,3-dimethylimidazolidine-2-thione(V) can serve as a good catalyst for the conversion of the ylide to the selenide and tetra-substituted ethylene. The details of scope and limitations of these reactions are being further examined now and will be published elsewhere soon.

Scheme 1.

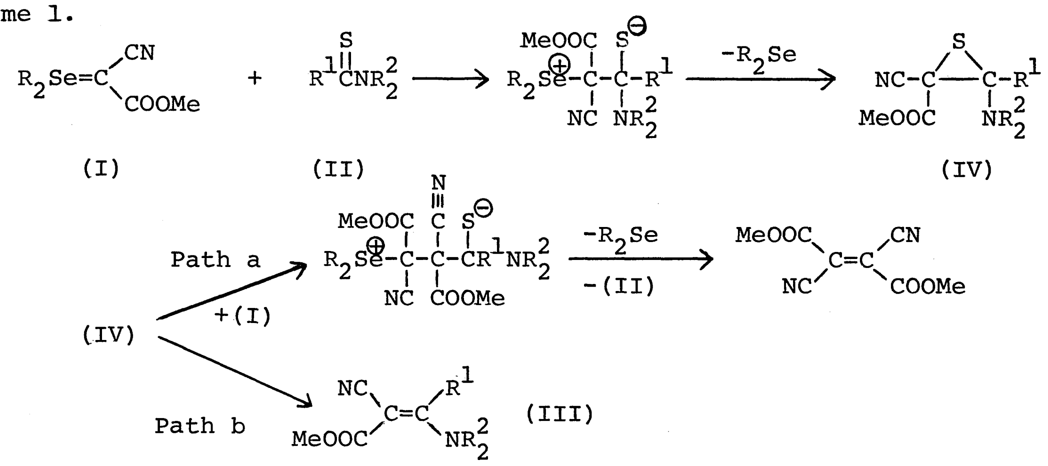
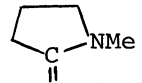
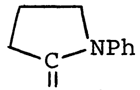
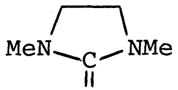
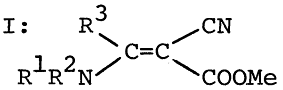


Table 1. Reactions of Dibenzylselenonium Cyano(methoxycarbonyl)methylide(I) with Different Thioamides(II) in $CHCl_3$ at Room Temperature

Thioamide (II)	[II]/[I]	Reaction time	Product (isolated yield,%) $(PhCH_2)_2Se$	III[a]	Olefin[b]	Recovered thioamide(%)
CH_3CSNMe_2	1	1 hr	81	0	23	24
	0.5	4 hr	89	0	38	c
	0.05	5 hr	75	0	69	0
 (II-Me)	1	10 min	87	87	trace	11
	0.1	5 hr	92	c	66	0
 (II-Ph)	1	10 min	78	24[9]	55	52
	1[d]	1 hr	84	32	16	47
	0.5	10 min	93	25	65	1
	0.2	1 hr	88	7.1	71	0
	0.1	5 hr	84	6.6	69	0
	0.05	5 hr	86	2.1	81	0
 (V)	1	10 min	72	c	71	73
	0.1	5 hr	92	c	87	0
CS_2	50	5 hr	82		41	

a) III: 
$(R^1R^2N)R^3C=C(CN)COOMe$ III-Me: R^1 = Me; R^2,R^3 = $(CH_2)_3$ III-Ph: R^1 = Ph; R^2,R^3 = $(CH_2)_3$

b) Dimethyl dicyanofumarate. c) Not determined. d) In 300 ml of $CHCl_3$.

References and Notes

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2) H. Matsuyama, H. Minato, and M. Kobayashi, Bull. Chem. Soc. Japan, 46, 3158(1973).

3) S. Tamagaki and I. Hatanaka, Chem. Lett., 301(1976).

4) C.J. Ireland and J.S. Pitey, J. Chem. Soc., Chem. Commun., 4(1972).

5) III-Me: m.p. 113-114°C; Found:C,59.89;H,6.64;N,15.54%. Calcd for $C_9H_{12}O_2N_2$:C,59.98;H,6.71;N,15.55%. NMR($CDCl_3$): δ 3.76(s,3H),3.55(m,4H), 3.49(s,3H),2.10(m,2H). IR(KBr): 2200, 1690 cm^{-1}.

6) R. Luckenbach, Synthesis, 307(1973).

7) M. Mikolajczyk, Chem. Ind.(London), 2059(1966).

8) R. Appel and W. Büchner, Ann. 618, 57(1968); Chem. Ber., 95, 855(1962).

9) III-Ph: m.p. 162-163°C; Found:C,69.35;H,6.41;N,12.01%. Calcd for $C_{14}H_{14}O_2N_2$:C,69.42;H,5.78;N,11.57%. NMR($CDCl_3$): δ 7.70(m,5H),3.91(m,4H), 3.91(s,3H),2.45(m,2H). IR(KBr): 2200, 1690 cm^{-1}.

(Received September 27, 1976)