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A NOVEL TETRAMETHYLTHIOUREA-CATALYZED DECOMPOSITION OF STABILIZED SELENONIUM YLIDES

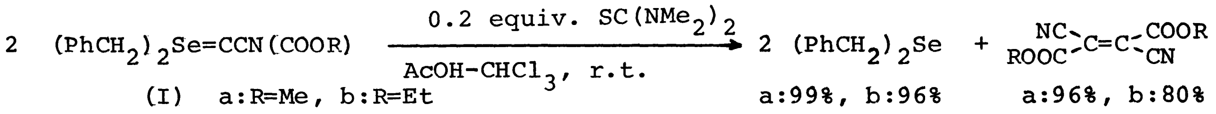
Seizo TAMAGAKI* and Isao HATANAKA
Department of Applied Chemistry, Faculty of Engineering,
Osaka City University, Sugimoto-cho, Sumiyoshi-ku,
Osaka 558

A few stabilized selenonium ylides react with a catalytic amount of tetramethylthiourea in the presence of acetic acid at room temperature to give the corresponding selenides and olefins in good yields.

Considerable effort has been devoted to studies of sulfonium and selenonium ylides.$^{1)}$ Particularly, much of attention has been directed toward the mechanism for the thermal decomposition of several non-isolable sulfur ylides to sulfides which are accompanied by olefins from the alkylidene portions of the starting ylides,$^{2)}$ but very few studies have been made on ylide decompositions which are promoted by the catalytic action of certain reagents to give the corresponding olefins.$^{3)}$

In this communication we wish to report a hitherto unknown type of facile thiourea-catalyzed decomposition of stable selenonium ylides to form the corresponding selenides and olefins.

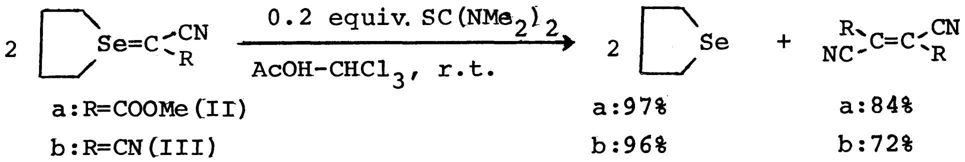
When one mmol of dibenzylselenonium cyano(methoxycarbonyl)methylide(I) which is quite stable at room temperature was treated with an equimolar amount of tetramethylthiourea in 5 ml of an acetic acid-$CHCl_3$ solvent(1:25, V/V) for 30 min at room temperature, the crystals of dimethyl dicyanofumarate$^{4)}$ precipitated in a 91 % yield from the solution because of its low solubility in the solvent used. Evaporation of the solvent from the filtrate and then thin-layer chromatographic separation of the resulting residue gave a 90 % yield of dibenzyl selenide, and over 80 % of the initially employed thiourea was recovered unchanged, suggesting that only less than 0.2 molar amount of the thiourea is sufficient to complete the reaction.



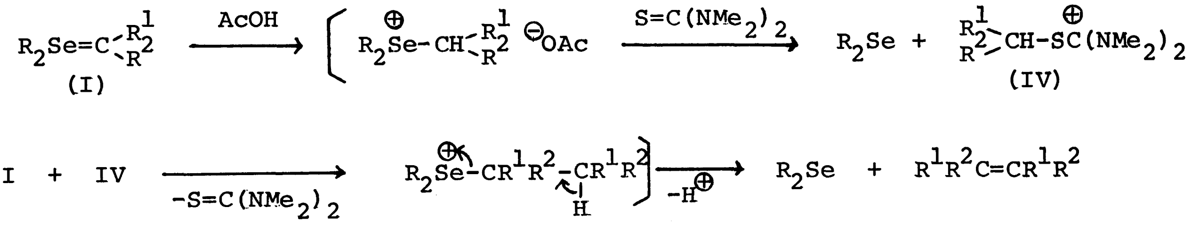
$$2\ (PhCH_2)_2Se{=}CCN(COOR) \xrightarrow[AcOH-CHCl_3,\ r.t.]{0.2\ equiv.\ SC(NMe_2)_2} 2\ (PhCH_2)_2Se + \overset{NC}{\underset{ROOC}{}}C{=}C\overset{COOR}{\underset{CN}{}}$$

(I) a:R=Me, b:R=Et　　a:99%, b:96%　　a:96%, b:80%

Similarly, the reaction of tetramethyleneselenonium cyano(methoxycarbonyl)-methylide(II) or dicyanomethylide(III) with 0.2 equiv of tetramethylthiourea was found to produce dimethyl dicyanofumarate or tetracyanoethylene in fairly good yields, respectively.



The data available at present does not permit an elucidation of a proper mechanism. However, the most plausible mechanism for the reaction could be depicted as follows.



Detailed mechanistic features of these reactions are now being examined in this laboratory and will be reported elsewhere in the near future.

References and Notes

1) S. Tamagaki, I. Hatanaka, and K. Tamura, Chem. Lett., 81(1976); S. Tamagaki and K. Sakaki, Chem. Lett., 503(1975); A.W. Johnson, "Ylid Chemistry," Academic Press, New York(1966).

2) E.J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 84, 3782(1962); ibid., 87, 1353(1965); A.W. Johnson and J.C. Williams, J. Amer. Chem. Soc., 86, 918(1964); V. Franzen and H.E. Diesen, Chem. Ber., 96, 1881(1963); C.G. Swain and E.R. Thornton, J. Amer. Chem. Soc., 83, 4043(1961); A.W. Johnson and R.B. LaCount, J. Amer. Chem. Soc., 83, 417(1960); E.D. Hughes and K.I. Kurian, J. Chem. Soc., 1601(1935).

3) H. Matsuyama, H. Minato, and M. Kobayashi, Bull. Chem. Soc. Japan, 46, 3158 (1973); B.M. Trost, J. Amer. Chem. Soc., 89, 138(1967).

4) C.J. Ireland and J.S. Pitey, J. Chem. Soc., Chem. Commun., 4(1972); K. Kudo, Bull. Chem. Soc. Japan, 35, 1490(1962); D.G.I. Felton and S.F.D. Orr, J. Chem. Soc., 2170(1955).

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