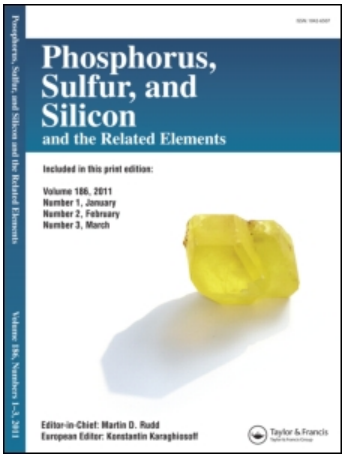


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE REARRANGEMENT OF ARYLSELENENAMIDES

P. T. Southwell-keely[a]; I. L. Johnstone[a]; E. R. Cole[a]
[a] School of Wool and Pastoral Sciences and the Department of Applied Organic Chemistry, The University of New South Wales, Kensington, N.S. W., Australia

To cite this Article Southwell-keely, P. T. , Johnstone, I. L. and Cole, E. R.(1976) 'THE REARRANGEMENT OF ARYLSELENENAMIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 1: 2, 261 — 262
To link to this Article: DOI: 10.1080/03086647608073330
URL: http://dx.doi.org/10.1080/03086647608073330

Phosphorus and Sulfur
1976, Vol. 1, pp. 261-262

THE REARRANGEMENT OF ARYLSELENENAMIDES

by

P. T. Southwell-Keely, I. L. Johnstone and E. R. Cole

From the School of Wool and Pastoral Sciences and the Department of Applied Organic Chemistry, The University of New South Wales, Kensington, N.S.W. 2033, Australia

Received March 22, 1974

ABSTRACT

Attempts to synthesize N-phenylbenzeneselenenamide always produced the isomeric *p*-aminodiphenyl selenide, probably as a result of an acid catalyzed rearrangement. The ease with which this rearrangement occurs is contrasted with the forcing conditions required for the analogous rearrangement of sulfenamides.

Much attention has been given to comparisons of the properties and biological activities of organosulfur and organoselenium compounds. Cases in point are methionine and selenomethionine. Less notice, however, appears to have been given to differences in reactivity.

Aryl sulfenamides may be conveniently prepared by the reaction of sulfenyl halides with amines according to the expression

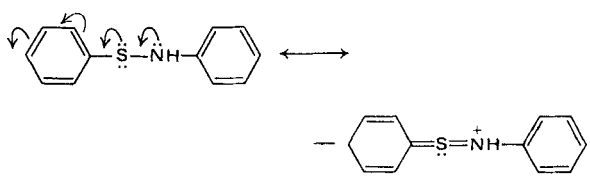
$$RSX + 2H_2NR' \rightarrow RS\,NH\,R' + R'NH_3^+X^-$$

The few selenenamides that have been prepared by this method are characterized by the presence of strong electron withdrawing groups in the ring carrying the selenium atom as illustrated by the stability of N-*p*-tolyl-*o*-nitrobenzeneselenenamide (**1**), N-phenyl-*o*,*p*-dinitrobenzeneselenenamide (**2**) and N-phenylanthraquinoneselenenamide (**3**).[1,2,3]

Present attempts to prepare N-phenylbenzeneselenenamide (**4**) by this reaction always gave the isomeric *p*-aminodiphenyl selenide (**5**) even when the reaction was carried out at low temperature (−80°). The question then arises as to whether the product **5** is the result of a rapid rearrangement of initially formed **4**.

Although the analogous sulfenamides are more stable, it has been shown that anilinium chloride promotes thermal rearrangement to isomeric *o*- and *p*-aminodiphenyl sulfides at a rate, and to an extent, dependent on concentration.[4] Moreover, if the synthesis of compounds **1** and **2** is attempted in chloroform solution using the selenenyl thiocyanate (RSeSCN) as reactant, products are the isomeric amino selenides.[3] Thus it seems that the byproduct of the reaction, anilinium thiocyanate, soluble in the solvent chloroform, is better able to catalyze the rearrangement to the extent of overcoming the stabilizing effects of the electron withdrawing groups. The ease with which rearrangement occurs under these conditions may be compared with conditions employed in the thermal (190°) rearrangement of unsubstituted sulfenamides, reduced (to 100°) in the presence of acid.[4]

One explanation of these results would relate to differences in the extent to which sulfur and selenium participate in stabilizing conjugative reactions. It would be expected that conjugation of the NH group with the alternate aromatic system would be stronger in the sulfenamides than with the selenenamides. This effect would impose the need for stronger acid catalysis in the rearrangement.

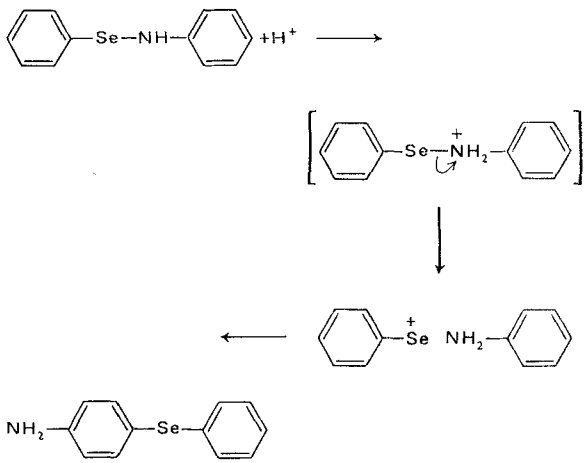


The lesser tendency of the $4(pz)^2$ electron pair of selenium to conjugate with an aromatic system has been inferred from dipole moments and from

1. O. Behagel and W. Müller, *Chem. Ber.*, 68, 1540 (1935).
2. W. S. Cook and R. A. Donia, *J. Am. Chem. Soc.*, 73, 2275 (1951).
3. H. Rheinboldt and M. Perrier, *Bull. Soc. Chim. Fr.*, 445 (1955).
4. F. A. Davis, E. R. Fretz and G. J. Horner, *J. Org. Chem.*, 38, 690 (1973).

dissociation constants of benzeneseleninic acids including the *p*-nitro derivative.[5]

A net result of this difference would be the need for stronger acid catalysis for the rearrangement of sulfenamides. By contrast only weak acid catalysis might be required to promote the appearance of the benzeneselenenyl cation as reactive entity from initially formed selenenamide.



Alternatively it is possible that **5** results from direct attack of the selenenyl halide on the aromatic nucleus of the amine following polarization of the selenium-halogen bond in the reagent. However this explanation must contend with the appearance of the selenenamide under other conditions and is probably less likely to apply.

5. J. Gosselck, *Angew. Chem., Int. Ed.*, **2**, 660 (1963).

Experimental Section

a) Benzeneselenenyl bromide (**6**). To a vigorously stirred solution of diphenyl diselenide (**7**) (0.45 g, 1 *M*) in chloroform (10 ml) was added dropwise a solution of bromine (0.24 g, 1 *M*) in chloroform (10 ml). A red precipitate formed and the mixture was allowed to stand for one hour before removal of the solvent *in vacuo*. Yield 0.66 g (97%).

b) Reaction of **6** with aniline. The crude **6** in ether (20 ml) was added dropwise to a vigorously stirred solution of aniline (0.52 g, 2 *M*) in ether (20 ml). After standing one hour aniline hydrobromide was filtered off and the solvent removed *in vacuo*.

The crude blue-green product in benzene (5 ml) was loaded on to a column of alumina (30 g, activity II) and the chromatogram developed with benzene/chloroform, 3 : 2.

Fraction 1 (10 ml) contained **7**. The product from fractions 2–4 was rechromatographed on a similar column using benzene as developing solvent. From the second of two reddish colored fractions was obtained (**5**) (0.19 g, 28%) which after several recrystallizations from aqueous ethanol, gave orange-red needles, mp 92–93° (lit.[6] 93–94°) ir (KBr) 3340 and 3430 cm^{-1} (NH_2); nmr ($CDCl_3$) δ 3.7 (NH_2).

Anal. Calc. for $C_{12}H_{11}NSe$: C, 58.10; H, 4.47; N, 5.64. Found C, 58.35; H, 4.75; N, 5.44.

6. W. R. Gaythwaite, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 2287 (1928).