Tetrahedron Letters No. 26, pp 2239 - 2242, 1978.
0040-4039/78/0622-2239$02.00/0

A NEW REARRANGEMENT OF N-ARYLHYDROXAMIC ACIDS CATALYZED BY SELENINIC ACIDS AND PHENYLSELENENYL CHLORIDE

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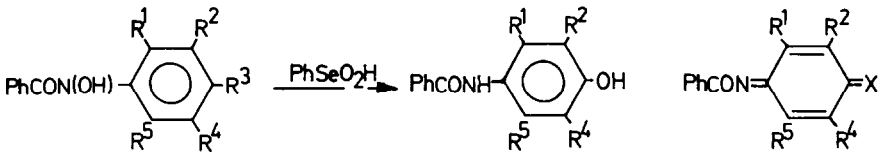
(Received in USA 19 December 1977; received in UK for publication 2 May 1978)

Catalytic amounts of seleninic acids and also selenium(II) species such as phenylselenenyl chloride promote rearrangement of N-arylbenzohydroxamic acids under very mild conditions to give p-hydroxy benzanilides, N-benzoyl p-quinoneimines or N-benzoyl p-quinolimines depending on the structure of the hydroxamic acids and the reaction conditions. In this paper we wish to present some of our preliminary results and a plausible mechanism for this rearrangement.

The experiments were performed by simply adding 0.05 eq. of phenylseleninic acid (or phenylselenenyl chloride) to a solution of the hydroxamic acid[3] (1 mmol) in methylene chloride (5 ml) at room temperature. The results are presented in Table 1. In all reactions varying amounts of the corresponding benzanilides (deoxygenation)* were also formed.[15]

Table 1



1a	R^1-R^5 = H	1b (70%)[a]	-
2a	R^2-R^4 = H; R^1,R^5 = CH_3	2b (60%)[a]	-
3a	R^1,R^3,R^5 = H; R^2,R^4 = CH_3	-	3b X = O (48%)[b]
4a	R^1,R^2,R^4,R^5 = H; R^3 = CH_3	-	4b X = CH_3,OH (30%)[c]

[a] 1b[5] and 2b (m.p. 241-2 °C) precipitated from the reaction mixtures and were almost pure without recrystallization from ethanol/water.

[b] Prep. TLC followed by recrystallization from $CHCl_3$/pentane (m.p. 114-116 °C).

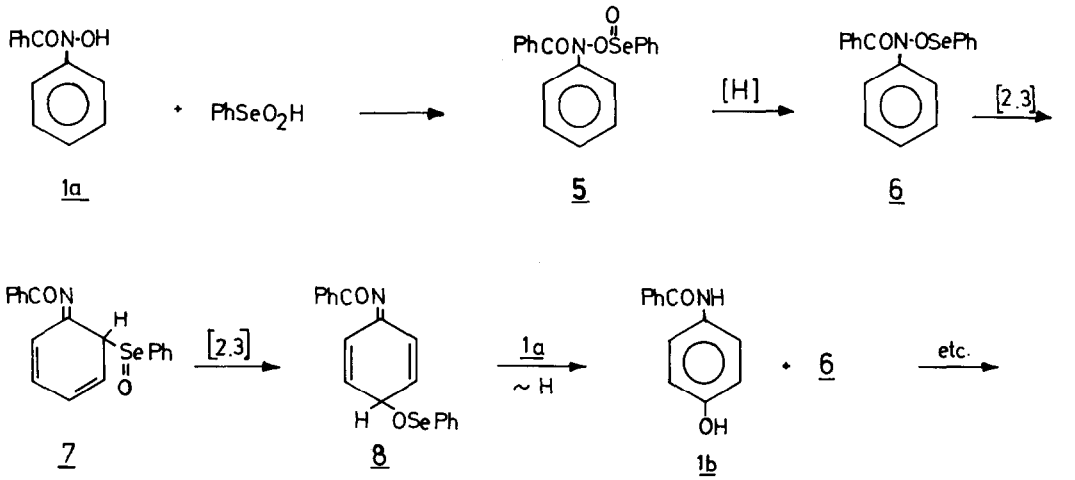
[c] Prep. TLC gave 4b as an oil (~ 90% purity NMR).

With 1a as substrate we have also performed the reaction with o-carboxyl phenylseleninic acid,[6] phenylselenenyl chloride and N-(phenylseleno)-succinimide[7] as catalysts. The first mentioned one seemed to be a more efficient catalyst since it gave a good yield of 1b even at

0.01 eq. (65%).[8] Phenylselenenyl chloride gave essentially the same result as did phenylseleninic acid while N-(phenylseleno)-succinimide was somewhat less efficient.

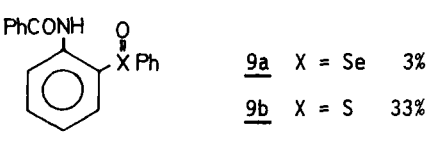
Control experiments showed that selenium dioxide did not catalyze the rearrangement, nor did phenylsulfenyl chloride, phenylsulfinic acid or p-toluenesulfonic acid. Thus, it seems likely that the reaction is not just an acid catalyzed displacement such as the Bamberger rearrangement[9] and it seems specific for the selenium reagents. It is interesting to note that a reaction mixture containing selenium dioxide and β-pinene did promote the rearrangement of 1a (yield 65% of 1b). Allylic seleninic acids are thought to be intermediates in the oxidation of olefins by selenium dioxide.[10]

Our favored mechanism for the rearrangement is shown in Scheme 1 and involves the initial formation of an O-seleninylhydroxamic acid 5, which we believe is reduced to the corresponding selenenylhydroxamic acid 6 by some as yet unknown reductant.



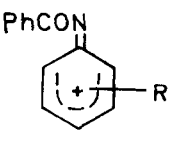
Scheme 1

Our arguments for a selenium(II) species 6 as intermediate are based on the following: a) the prevention of the rearrangement by a small amount of hydrogen peroxide (in eq. amount to the seleninic acid); b) the catalytic action of the selenium(II) species phenylselenenyl chloride and N-(phenylseleno)succinimide; c) and the formation of 2-phenylselenoxy benzanilide (9a)[11] when the reaction was performed with phenylselenenyl chloride and 1a in the presence of triethylamine at low temperature. Similarly 2-phenylsulfoxybenzanilide (9b)[11] was formed when phenylsulfenyl chloride was used instead of phenylselenenyl chloride.



9a X = Se 3%

9b X = S 33%



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Selenium(IV) compounds are very easily reduced to selenium(II) compounds, thus a variety of reductants could serve to get the catalytic cycle started (i.e. 5 → 6 in Scheme 1) when a seleninic (IV) acid is used as catalyst. The complete inhibition of the rearrangement in the presence of a few percent of an oxidant (e.g. H_2O_2) is, in our opinion, a key observation supporting the proposed mechanism. It provides strong evidence against the involvement of seleninic ester 5 in the rearrangement process. This would appear to rule out [3.3] type rearrangements so elegantly studied by Oae and Sakurai in related hydroxamic acid derivatives.[12] This same line of evidence also speaks against ionic mechanisms[13] since the selenium(IV) ester 5 should be much more reactive in an ionic process than the selenium(II) ester 6. Further evidence against an ionic mechanism (with intermediates such as 10) is that when the rearrangement was performed in the presence of 16 equivalents (0.5 ml in 4.5 ml CH_2Cl_2) of methanol, no p-methoxy benzanilide was found.[14] The reaction was considerably slower in the presence of methanol (for an ionic process one might have expected it to be faster) but the yield of 1b (and 2b) was still 65% after 3 h. In those cases where ionic mechanisms have been proposed there is substantial ortho-substitution.[13] Ortho-substitution was not observed in the present case. Thus all evidence seems to support an intramolecular mechanism for this selenium catalyzed rearrangement.

Acknowledgements. We are indebted to the Swedish Natural Science Research Council (T.F.), the National Science Foundation (CHE74-21260), the National Institutes of Health (GM 21686) and Hoffmann-LaRoche, Inc. for financial support.

References and Notes

1. Post doctoral fellow M.I.T. 1976-1977. Present address: Organic Chemistry 1, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund, Sweden.
2. Present address: Department of Chemistry, Stanford University, Stanford, California 94305, U.S.A.
3. N-Phenylhydroxamic acid (1a) was obtained from Eastman-Kodak and the other three (2a-4a) were prepared from benzoyl chloride (1 eq.) and the respective hydroxylamine (2 eq.) in methylene chloride. M.p. 2a: 161-162 °C; 3a: 90-91 °C and 4a: 110-110.5 °C. Yields 50-70%. Satisfactory elemental analyses were obtained for all new compounds except for 4b.
4. Deoxygenation of 1a is also catalyzed by $VO(acac)_2$: Steve Current and K. Barry Sharpless: unpublished.
5. G.T. Tissue, M. Grassmann and W. Lwowski, Tetrahedron 24, 999 (1968).
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7. This hitherto unknown compound was recently prepared in our laboratory by Dr. T. Hori.
8. At the 0.01 eq. level phenylseleninic acid gave only 18% yield of 1b.
9. Y. Yukawa, J. Chem. Soc. Japan Pure Chem. Sect. 71, 547 (1950). H.F. Heller, E.D. Huges and C.K. Ingold, Nature 168, 909 (1951).
10. K.B. Sharpless and R.F. Lauer, J. Am. Chem. Soc. 94, 7154 (1972); D. Arigoni, A. Vasella, K.B. Sharpless and H.P. Jensen, ibid. 95, 7917 (1973); H.P. Jensen and K.B. Sharpless, J. Org. Chem. 40, 264 (1975).

11. a) Authentic substances were prepared by the $NaIO_4$ oxidation of the corresponding selenide[11b] and sulfide[11c] in THF/H_2O. M.p. 9a: 142-144 °C; 9b: 101-102 °C; b) O. Behagel and K. Hoffmann, Chem. Ber. 72B, 582 (1939) prepared o-phenylselenoaniline. From this compound and benzoyl chloride we prepared the benzanilide. M.p. of o-phenylselenobenzanilide 83-83.5 °C; c) R. Adams, W. Reifschneider and M.D. Nair, Croat. Chem. Acta 29, 277 (1957).

12. S. Oae and T. Sakurai, Tetrahedron 32, 2289 (1976).

13. a) J.D. Scribner, J.A. Miller and E.C. Miller, Cancer Res. 30, 1570 (1970); b) J.D. Scribner, J. Org. Chem. 41, 3820 (1976); c) T. Okamoto, K. Shudo and T. Ohta, J. Am. Chem. Soc. 97, 7184 (1975); d) P.G. Gassman and G.A. Campbell, J. Am. Chem. Soc. 93, 2567 (1971).

14. This type of experiment has been used (see ref. 9) to establish the intermolecular nature of the Bamberger rearrangement.

15. These deoxygenation products probably arise by [2.3] rearrangement of the selenium (II) ester intermediate (e.g. 6) to the carbonyl oxygen. This path might be expected to compete with the [2.3] rearrangement to carbon (6 → 7) shown in Scheme I.