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A Seleno-Pummerer Rearrangement of Haloselenuranes

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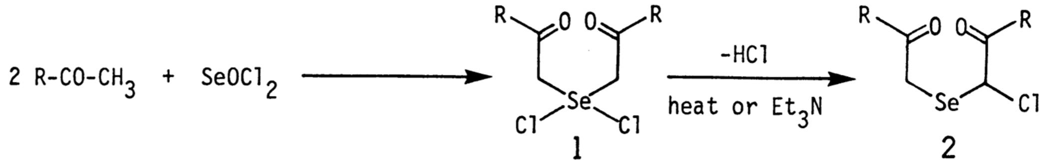
When heated or treated with triethylamine in tetrahydrofuran, diacetonyl- and diphenacylselenium dichlorides and their derivatives undergo seleno-Pummerer rearrangement to give the corresponding α-chloro selenides in good yields.

Pummerer rearrangement has been extensively studied both from mechanistic and synthetic points of view.[1] In spite of the recent explosive growth of the chemistry of organoselenium compounds, seleno-Pummerer rearrangement has not been much stuided. It is only known that oxyselenuranes, formed either by reaction of selenoxides with acid anhydrides[2,3] or by action of benzoyl peroxide on selenides,[4] undergo Pummerer rearrangement to give the corresponding α-acyloxy selenides. Herein we report the seleno-Pummerer rearrangement of diacetonyl- and diphenacylselenium dichlorides and their derivatives (1) to give the corresponding α-chloro selenides (2) in good yields. The reaction corresponds to the Pummerer rearrangement involved in the α-chlorination of sulfides by chlorinating reagents such as molecular chlorine, sulfuryl chloride or iodobenzene dichloride.[1]

The dichlorides 1 are easily obtained in high yields by reaction of 2 equiv. of ketones with selenium oxychloride[5,6] or selenium tetrachloride.[7]



1

2

Heating diphenacylselenium dichloride (1a) in refluxing tetrahydrofuran (THF) for 1 h affords the chloro selenide 2a (65%), phenacyl chloride (18%),[8] and a small amount of acetophenone. Probably 1a partly exists as an ionized species 1a' in a solution. Thermal dehydrochlorination of 1a' leading to the carbonyl-stabilized selenium ylide 3 followed by migration of chlorine would give rise to 2a. Phenacyl chloride must be formed from 1a' through the C-Se bond cleavage by chloride ion, which is rather commonly observed with diorganylselenium dihalides.[9] The action of base on 1a is expected to facilitate the dehydrochlorination. Actually treatment of 1a with a slight excess of triethylamine in THF at 0 °C for 3 h cleanly afforded 2a in 86% yield.[10,11]

A series of 1 were synthesized and treated with slightly excess triethylamine in THF at 0 °C for 3 h. The results summarized in Table 1 show that the reaction is general and affords the corresponding 2 in good yields. Recently synthetic use

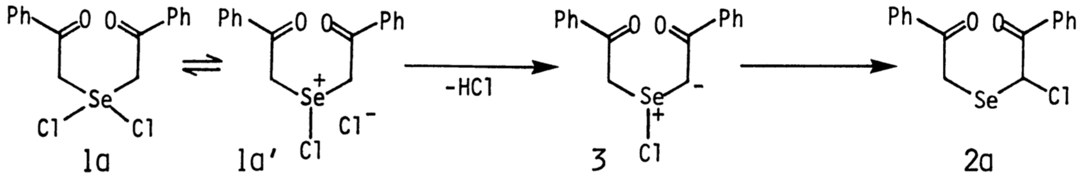
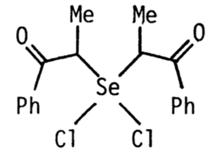


Table 1. Et_3N-induced Seleno-Pummerer Rearrangement of 1 to 2

R	2: Yield/%	R	2: Yield/%	R	2: Yield/%
C_6H_5	86	2-Thienyl	77	Me	69
$4\text{-}MeC_6H_4$	92	$4\text{-}MeOC_6H_4$	77	Me_3C	90

of diphenacyl selenide and related compounds has been developed[6,12] and hence compounds 2, being readily obtainable here, might serve as useful synthetic intermediates.

Finally, treatment of compound 4 having methyl groups on α-positions with triethylamine in THF at 0 °C unexpectedly but cleanly afforded phenyl vinyl ketone in 85% yield. In this case the transition state of E2 elimination (shown below) seems to be kinetically preferable to that leading to the selenium ylide as the intermediate of Pummerer rearrangement.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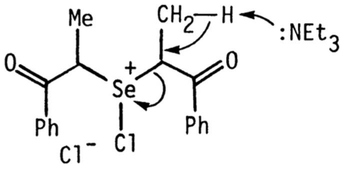

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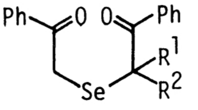
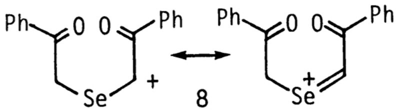
1) E. Block, "Reactions of Organosulfur Compounds," Academic Press, New York (1978), p. 154.
2) C. Paulmier, "Selenium Reagents and Intermediates in Organic Synthesis," Pergamon Press, Oxford (1986), p. 128.
3) H. Hevesi, "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai and Z. Rappoport, John Wiley, New York (1986), Vol. 1, p. 315.
4) Y. Okamoto, K. L. Chellappa, and R. Homsany, J. Org. Chem., 38 3172 (1973).
5) R. E. Nelson and R. N. Jones, J. Am. Chem. Soc., 52, 1588 (1930).
6) J. Nakayama, M. Shibuya, and M. Hoshino, Heterocycles, 26, 909 (1987).
7) Fr. Kunckell and R. Zimmermann, Liebigs Ann. Chem., 314, 281 (1901).
8) It was reported that heating 1a and related compounds in boiling benzene or without solvent gives phenacyl chloride and related chlorides in 41-58% yields; J. P. Schaefer and F. Sonnenberg, J. Org. Chem., 28, 1128 (1963). These authors may have overlooked the formation of products of Pummerer rearrangement because product isolation was done by distillation.
9) Ref. 2, p. 102.
10) Treatment of 1a with p-toluenesulfonamide also affords 2a as the major product. No expected N-tosyl selenilimine was formed.
11) Treatment of 1a with triethylamine in the presence of methanol affords 2a (36%), 5 (12%), 6 (12%), and 7 (34%). The formation of 6 may suggest that rearrangement of 3 to 2a occurs via the carbocation intermediate 8 (6 is not formed from 2a and methanol).
12) J. Nakayama, Y. Ikuina, F. Murai, and M. Hoshino, J. Chem. Soc., Chem. Commun., 1987, 1072; J. Nakayama, F. Murai, M. Hoshino, and A. Ishii, Tetrahedron Lett., 29, 1399 (1988); J. Nakayama and Y. Sugihara, J. Phys. Org. Chem., 1, 59 (1988).



5: $R^1=R^2=Cl$
6: $R^1=OMe$, $R^2=H$
7: $R^1=R^2=H$



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