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"Selenium Polonovski Reaction" Using Benzeneselenenyl Triflate

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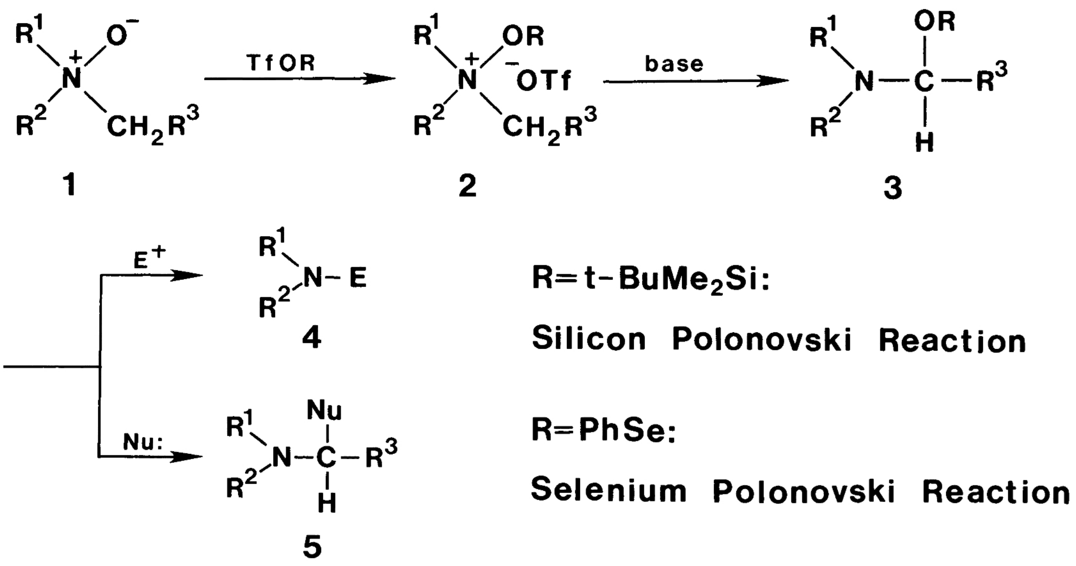
Selenoxyammonium salts prepared from tertiary amine N-oxides and benzeneselenenyl triflate undergo rearrangement in the presence of triethylamine or DBU to give α-selenoxyamines, which react in situ with an electrophile or nucleophile to afford new secondary or tertiary amine derivatives.

We previously reported[1)] "silicon Polonovski reaction" using trialkylsilyl triflate (Scheme 1; R=t-BuMe$_2$Si).[2)] Although this reaction is useful for functional conversions in tertiary amines, it requires a very strong base, i.e., alkyllithium, to induce 1,2-shift of an RO group from nitrogen to α-carbon (i.e., **2**→**3**). In continuation of our work on amine N-oxides we have recently found that such weaker bases as triethylamine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), compatible with many functional groups, can induce the rearrangement when benzeneselenenyl triflate (PhSeOSO$_2$CF$_3$; BST) is used instead of trialkylsilyl triflate. A very recent communication by Murata and Suzuki[3)] on the preparation and use of BST in selenolactonization prompts us to report our own preliminary results on the use of BST in "selenium Polonovski reaction" (Scheme 1, R=PhSe).

A dichloromethane solution of BST can be prepared by the following two methods:

(1) An equimolar amount of silver triflate and benzeneselenenyl chloride is mixed in dichloromethane at -15 °C to give a dark green suspension of BST (designated as BST-A).[4)]

(2) A mixture of neat triflic acid (a small excess) and benzeneselenenyl chloride is heated at 60 °C for 1 h. Hydrogen chloride is evolved to give a dark green



Scheme 1.

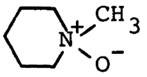
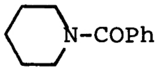
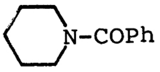
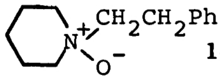
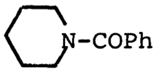
liquid. Hydrogen chloride and an excess of triflic acid are removed under reduced pressure and the residue is dissolved in dichloromethane (designated as BST-B).5) The dichloromethane solution of BST-B thus prepared can be stored at room temperature at least for several weeks if it is protected from moisture and light.

Treatment of amine N-oxides with the dichloromethane solution of BST-A or BST-B followed by sequential reactions with triethylamine (or DBU) and benzoyl chloride gave the corresponding benzamide (**4**; E=COPh). The results are summarized in Table 1. Both BST-A and BST-B give similar results. BST-B is a reagent of choice since, as mentioned above, its dichloromethane solution can be stored for a long time without any deterioration and furthermore it can avoid the use of rather expensive silver triflate.6)

The use of other nucleophiles instead of benzoyl chloride enables a similar transformation into other types of secondary and tertiary amine derivatives. Thus, reactions of N-methylpiperidine N-oxide (**1d**) with phenyl chloroformate or benzyl chloride under similar conditions afforded N-phenoxycarbonylpiperidine (**4**: $R^1R^2=(CH_2)_5$, $E=CO_2Ph$; 41% (BST-B)) or N-benzylpiperidine (**4**: $R^1R^2=(CH_2)_5$, $E=CH_2Ph$; 46% (BST-B)).

The selenium Polonovski reaction is also applicable to a reaction with an electrophile. For example, **3d** obtained from **1d** using BST-B is reacted with triethylaluminium (hexane solution) as an electrophile to gave N-propylpiperidine

Table 1. Conversion of Amine N-Oxides into the Corresponding Benzamides[a)]

N-Oxide	BST[b)]	Base	Amide	Yield/%[c)]	
$(PhCH_2)_3N^+$-O^- **1a**	A	DBU	$(PhCH_2)_2NCOPh$	50	
			$PhCH_2NHCOPh$	39	(89)
1a	A	Et_3N	$(PhCH_2)_2NCOPh$	48	
			$PhCH_2NHCOPh$	38	(86)
$(PhCH_2)Me_2N^+$-O^- **1b**	A	DBU	$(PhCH_2)MeNCOPh$	65	
			Me_2NCOPh	8	(73)
(cyclo-Hex)Me_2N^+-O^- **1c**	A	DBU	(cyclo-Hex)MeNCOPh	64	
			Me_2NCOPh	11	(75)
 **1d**	A	Et_3N		61	
1a	B	Et_3N	$(PhCH_2)_2NCOPh$	59	
			$PhCH_2NHCOPh$	18	(77)
1d	B	DBU		65	
1d	B	Et_3N		57	
 **1e**	A	DBU		66	

a) A typical procedure follows. Amine N-oxide (2 mmol) in dichloromethane is added to a dichloromethane solution (1.2-1.4 equiv.) of BST-A or BST-B at -78 °C. After the temperature of the mixture is gradually raised to 40 °C, triethylamine or DBU (1.5-2.0 equiv.) is added and the solution is kept at this temperature for 1 h. To this is added benzoyl chloride (2 equiv.) and the solution is heated for another 2 h. b) A: BST-A; B: BST-B. c) Values in parenthese are total yields.

(**5**: $R^1R^2=(CH_2)_5$, R^3=H, Nu=Et, 32%).

In summary we have prepared hitherto unknown[3)] benzeneselenenyl triflate (BST) by two different methods. The selenium Polonovski reaction using BST and amines as base provides a new convenient method for dealkylation, transalkylation, and functionalization of α-carbon in tertiary amines. It has the advantage over the silicon Polonovski reaction[1] in that it can be conducted by much weaker bases compared with the latter reaction which requires alkyllithiums.

Further application of this reaction and the optimization of the reaction conditions are now in progress.

References

1) R. Okazaki and N. Tokitoh, J. Chem. Soc., Chem. Commun., 1984, 192; N. Tokitoh and R. Okazaki, Tetrahedron Lett., 25, 4677 (1984); Chem. Lett., 1984, 1937; 1985, 241.

2) For reviews on Polonovski reactions, see G. A. Russel and J. G. Mikol, "Mechanism of Molecular Migrations," ed by B. S. Thyagarajan, Interscience, New York (1968), Vol. 1, p. 176; A. R. Katritzky and J. N. Lagowski, "Chemistry of Heterocyclic N-Oxides," Academic Press, New York (1971), pp. 279 and 362; M. Ikeda and Y. Tamura, Yuki Gosei Kagaku Kyokai Shi, 38, 10 (1980).

3) S. Murata and T. Suzuki, Chem. Lett., 1987, 849.

4) The solution must be used as such without filtration of silver chloride formed. The supernatant of the solution is capable of effecting "selenium Polonovski reaction" but in much poorer yields. Therefore the heterogenous solution of BST-A cannot be used as a stock solution. Although the effect of silver chloride is not clear at present, the reaction probably occurs on the surface of silver chloride.

5) The solution contains about 30% of selenanthrene as a side product, which does not affect the reaction although one must use the corresponding excess amount of the reagent.

6) The same reaction can be conducted also by benzeneselenenyl chloride or N-phenylselenophthalimide,[7] but the yields are much lower. For example, under similar conditions, **1a** and **1d** gave the corresponding benzamides in 22 and 15% yields respectively.

7) K. C. Nicolaou, D. A. Claremon, W. E. Barnette, and S. P. Seitz, J. Am. Chem. Soc., 101, 3704 (1979).

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