

REACTIONS OF AROMATIC NITRO, NITROSO, HYDROXYLAMINO  
AZOXY, AZO AND HYDRAZO COMPOUNDS WITH SELENOL<sup>1)</sup>

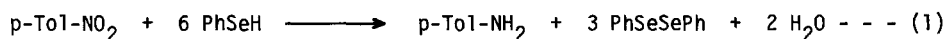
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Relative reactivities of aromatic nitro, nitroso, hydroxylamino, azoxy, azo and hydrazo compounds in the reduction with  $RSe^-$  were found to fall in the following order :  
 $R-N=O \gg R-N=N-R > R-NH-OH > R-\overset{O}{\underset{|}{N}}=N-R \approx R-NO_2 \gg R-NH-NH-R$ .

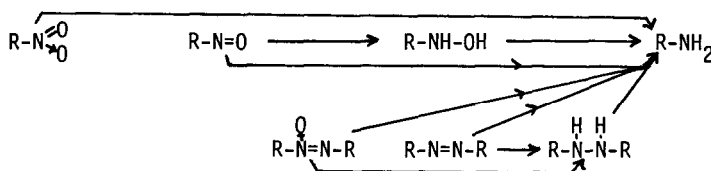
In the previous paper we reported the reactions of  $sp^2$  hybridized nitrogen with various nucleophiles including hydroxide, amines and 0,0-diethyl dithiophosphoric acid revealing that the reaction is orbital controlled<sup>2)</sup> and 0,0-diethyl dithiophosphoric acid is an excellent reducing agent.<sup>3)</sup> We now have investigated the reactions of nitro- and azoxyarene and related compounds with selenol, a very soft nucleophile, which was already reported by Günther to be capable of reducing azobenzene and disulfide to hydrazobenzene and thiol, respectively.<sup>4)</sup>

All the reactions were carried out in evacuated sealed NMR tubes using  $CDCl_3$  as solvent. The reaction between p-nitrotoluene and selenophenol took place smoothly to afford p-toluidine quantitatively at 100° (1 day). The reduction of unsaturated organic nitrogen compounds is known to involve an electron transfer from the reducing agent to the substrate in many cases, e.g. reductions of nitrobenzene with alkali sulfide<sup>4)</sup> and of nitrosobenzene with thiophenolate anion.

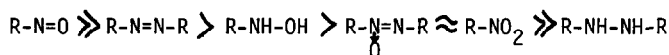


Since selenophenoxide anion is a much potent electron donor than its conjugate acid, diazabicyclo [2,2,2]octane (DABCO) was added to the reaction system as the base catalyst to generate  $PhSe^-$ . The reaction (1) was accelerated extremely by DABCO and proceeded at 35° (1 day). During the reaction none of the possible intermediates, p-nitrosotoluene and N-(p-tolyl)hydroxylamine, were detected, indicating that further reduction of the intermediates is faster than that of p-nitrotoluene. Actually this was confirmed by several experiments for each one of all the substrates. p-Nitrotoluene gave 4,4'-dimethylazoxybenzene quantitatively upon treatment with an equimolar amount of selenophenol, while N-(p-tolyl)hydroxylamine was obtained similarly by the reaction with 2 equimolar amounts of selenophenol.

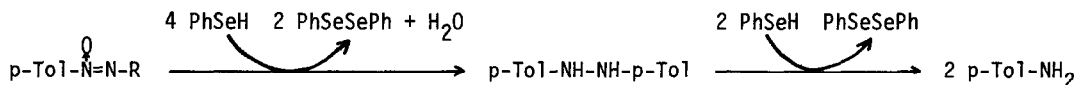
Scheme 1. Summary of the Reduction of Organic Nitrogen Compounds with Selenophenol



Relative Reactivities toward Selenophenoxide Anion (PhSeH + DABCO in  $\text{CDCl}_3$ , R = p-tolyl):



The reduction of 4,4'-dimethylazoxybenzene with selenophenol alone proceeded at  $100^\circ$  affording p-toluidine quantitatively after 1 day. The first step of this reaction was also found to be



of base catalyzed and took place at  $35^\circ$  affording 4,4'-dimethylhydrazobenzene quantitatively, even in the presence of excess selenophenol. DABCO, however, retarded further reduction of 4,4'-dimethylhydrazobenzene to p-toluidine. 4,4'-dimethylazobenzene was found to be converted readily to 4,4'-dimethylhydrazobenzene quantitatively even at  $25^\circ$  and no further reduction took place in the presence of DABCO. However, when 4,4'-dimethylazobenzene was treated with selenophenol alone without the base, 4,4'-dimethylhydrazobenzene was formed slowly at  $25^\circ$  and eventually reduced completely to p-toluidine upon heating at  $70^\circ$ . All the reactions which have been found to proceed quantitatively are summarized in Scheme 1.

Base catalyzed reactions of nitro, nitroso, azoxy and azo compounds with benzylselenol gave in substantial yields toluene which is undoubtedly originated from benzylselenol. Since  $\text{PhCH}_2\text{Se}^-$  is known to collapse readily to give elemental selenium and  $\text{PhCH}_2\cdot$ <sup>6)</sup> which can easily abstracts hydrogen from the selenol to form toluene, the formation of toluene in this reaction suggests the intervention of some electron transfer process from  $\text{PhCH}_2\text{Se}^-$  to the substrate giving  $\text{PhCH}_2\text{Se}\cdot$  in the course of the base catalyzed reactions of these substrates with benzylselenol.

#### REFERENCES

- 1) Reduction with Organic Selenium Compounds I.
- 2) S. Oae, N. Asai and K. Fujimori, *J. Chem. Soc., Perkin II*, 571, 1124 (1978).
- 3) S. Oae, N. Tsujimoto and A. Nakanishi, *Bull. Chem. Soc. Jpn.*, **46**, 535 (1973).
- 4) W. H. H. Günther, *J. Org. Chem.*, **31**, 1201 (1966).
- 5) S. Hashimoto, J. Sunamoto and A. Aoki, *Bull. Chem. Soc., Jpn.*, **40**, 2876 (1976).
- 6) F. J. Smentowski, *J. Amer. Chem. Soc.*, **85**, 3036 (1963).
- 7) J. Y. C. Chu and D. G. March, *J. Org. Chem.*, **41**, 3204 (1976).

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