Twofold Extrusion Reactions of Selones and Azides: the Preparation of Very Sterically Hindered Imines

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The twofold extrusion reaction of a selone with an aromatic azide is a useful method for the preparation of sterically hindered imines.

The preparation and reactions of very sterically hindered molecules are currently topics of great interest.[1] Quite often commonly used reactions when applied to very hindered molecules fail to effect the desired transformation or take a completely different course owing to steric constraints. In our continuing investigations into the reactivity of sterically hindered molecules we required very sterically hindered imines which could not be obtained by the normal condensation reaction of an amine with a ketone, even under forcing conditions.

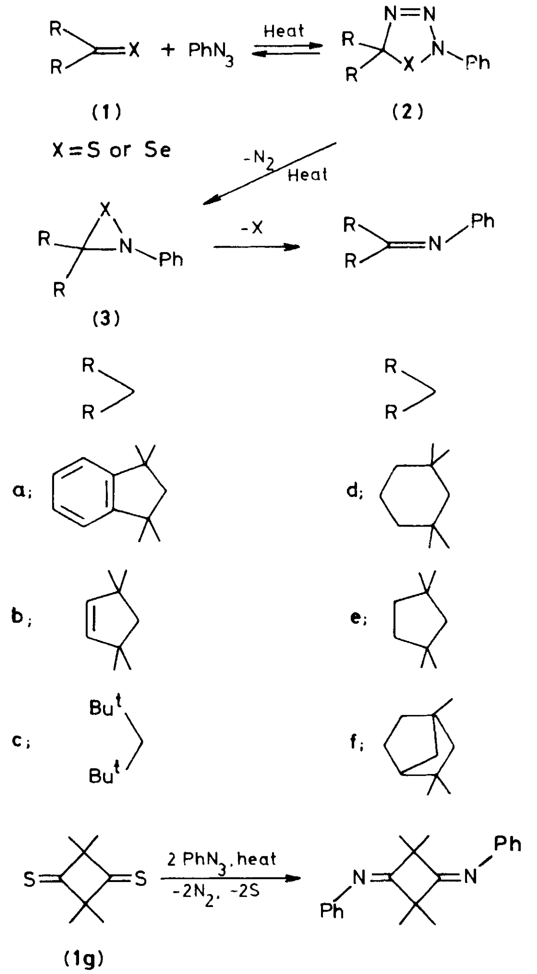
One reported method for the preparation of imines utilizes the reaction of a thione with an aromatic azide affording the desired imines in undetermined yields.[2] This reaction is an analogue of the twofold extrusion preparation of very sterically hindered olefins from thiones or selones and diazo compounds,[3,4] and should therefore be applicable in the preparation of very sterically hindered imines. The ready availability of sterically hindered thiones[3] and selones[4,5] would allow for a thorough investigation of the preparative utility of such an extrusion reaction, and also for a comparison of the relative reactivities of the thiones and selones in this cycloaddition and extrusion.

Treatment of a sterically hindered thione or selone with phenyl azide at 40—50 °C in benzene under nitrogen affords the corresponding *N*-phenylimines in good to excellent yields (Table 1). Analogous to the reaction with diazo compounds, the selones proved to be more reactive,[4] requiring lower

Table 1. Preparation of *N*-phenylimines.[a]

Thione or selone (**1**)	X	% Yield of imine[b]	Imine (m.p.) b.p.
a	S	70[c]	(119·5—122 °C)
	Se	100 (50)[d]	60 °C at 0.6 mmHg (subl.)
b	S	35	(44—47 °C)
	Se	100 (90)[d]	45 °C at 0.7 mmHg (subl.)
c	S	55	50 °C at 2 mmHg
	Se	80 (71)[d]	
d	S	52	40 °C at 0.7 mmHg
	Se	100 (86)[d]	
e	S	82	40 °C 0.5 mmHg
	Se	100 (63)[d]	
f	S	20	[e]
	Se	(94)[c,d]	
g	S	70[g]	[f]

[a] Satisfactory elemental analysis and spectra were obtained for these compounds. [b] Conversion determined by g.c. [c] Corrected for recovered starting materials. [d] (Isolated yield of pure product). [e] P. Lipp and G. Stutzinger, *Chem. Ber.*, 1932, **65B**, 241. [f] R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, 1961, **26**, 4340. [g] Compound (**1g**) is a dithione which affords a di-imine.



reaction temperatures and shorter reaction times. In addition, cleaner, less complex mixtures of products were obtained in the selone reactions, allowing for easier isolation of the desired imines.

The mechanism of this reaction is also intriguing. Presumably the reaction involves an initial cycloaddition between an azide and thione or selone (**1**), followed by extrusion of nitrogen and elemental sulphur or selenium, respectively. It was noted in monitoring certain reactions that while crude reaction mixtures might contain no phenyl azide, raising the reaction temperature regenerated the azide. This suggests a pre-equilibrium cycloaddition reaction forming a relatively stable 2,5-dihydro-thia- or -selena-triazole (**2**) which can retrocyclize as well. In other reactions extrusion of nitrogen was observed long before the onset of selenium extrusion, and selenium extrusion continued long after nitrogen evolution had ceased, suggesting the possibility of a moderately stable azathiirane or azaselenirane (**3**).

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