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Carbonylation of Selenilimines to Arylsulfonyl Isocyanates

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Abstract: Selenilimines of general formula $ArSO_2N{=}SePh_2$, **1**, can be catalytically carbonylated to arylsulfonyl isocyanates, **2**, in the presence of palladium complexes as catalysts. This transformation represents a new two-step oxidative N-carbonylation reaction.

Carbonylations taking place at nitrogen atoms in the presence of noble metal or selenium-based catalysts have been the subject of continuous interest[1,2,3] in the past decades. Our efforts to find new methods for the preparation of arylsulfonyl isocyanates, valuable intermediates in the synthesis of low-dose herbicides[4], have led to the discovery of novel catalytic reactions providing these compounds via carbonylation of N-chloroarylsulfonamidates[5], **3**, and (arylsulfonyliminoiodo)benzenes[6], **4**.

Now we report on a novel carbonylation of selenilimines **1** to arylsulfonyl isocyanates **2**, catalyzed by palladium complexes like $PdCl_2(PhCN)_2$ or $PdCl_2(CH_3CN)_2$ (eq. 1).

$$\underset{\mathbf{1}}{ArSO_2N{=}SePh_2} + CO \xrightarrow[35\ \text{bar},\ 50\ \text{C}]{\text{Pd-complex}} \underset{\mathbf{2}}{ArSO_2NCO} + Ph_2Se \qquad (1)$$

Selenilimines **1** were prepared from Ph_2Se and N-chloroarylsulfonamidates[7] or via addition of $ArSO_2NH_2$ to a solution of diphenylselenide dimethoxide[8]. The latter method proved to be especially useful in the preparation of **1c** and **1d**, which are not accessible via other known synthetic routes[9].

The carbonylation was accompanied by a CO pressure drop allowing to calculate a one to one molar ratio of the CO and the selenilimine. The formation of **2a** was undoubtedly proved by the $\nu_{as}NCO$ band at 2230 cm^{-1} appearing in the IR spectrum of the diluted reaction mixture . The yields of sulfonyl isocyanates prepared via reaction 1 and the analytical data of the 1-arylsulfonyl-3-arylureas, **5**, isolated upon addition of an amine reactant (2-chloroaniline (2-CA) or 2-amino-4-methoxy-6-methyl-1,3,5-triazine ($TANH_2$)) to the carbonylated reaction mixture are collected in Table 1.

Reaction 1 is the third example of catalytic N-carbonylations[5,6] which cannot be classified either as oxidative or reductive, discovered earlier for aromatic amines and nitro compounds. The chemistry involved in this transformation is best depicted as a two-step oxidative carbonylation in which the oxidation of the amino group and the carbonylation of the intermediate imine are carried out as isolated steps.

The starting materials **1**, **3** and **4** have certain common properties that may be connected with their ability to undergo catalytic carbonylation. Such features are their capability to transfer a sulfonylimino moiety to nucleophiles like phophines and sulfides or the low (~1260 cm^{-1}) $\nu_{as}SO_2$ frequencies[10] and the oxidative behaviour toward acidic KI solutions. On the contrary, attempted carbonylation of the phosphinimine $TsN{=}PPh_3$ did not afford any sulfonyl isocyanate and the unchanged substrate was recovered upon carbonylation. Notably, the phosphinimine displays $\nu_{as}SO_2$ absorption at 1267 cm^{-1} but is characterized by the complete lack of oxidative power. The carbonylation of selenilimines represents an important step in understanding the criteria for the right selection of substrates that undergo two-step oxidative N-carbonylation. A different relationship of structural features with the reactivity of nitrenoids to provide isocyanates has been recently discussed in connection with Hofmann-type reactions[11].

Table 1: Carbonylation of selenilimines to arylsulfonyl isocyanates

Carbonylated substrate **1**	Amine reactant	Yield of **2** (%)	Physical data of **2** and **5**
a	2-CA	64	**2a**: IR (CH_2Cl_2, cm^{-1}) 2230 **5a**: IR (KBr, cm^{-1}) 1698, 1599, 1444, 1353, 1160 MS-FAB : 325 $(M+H)^+$
b	2-CA	52	**2b**: IR(CH_2Cl_2, cm^{-1}) 2230 **5b**: IR (KBr, cm^{-1}) 1690, 1535, 1435, 1335, 1155 MS-FAB : 345 $(M+H)^+$
c	$TANH_2$	70	**5c**: IR (KBr, cm^{-1}) 1730, 1708, 1592, 1558, 1454, 1363, 1175
d	$TANH_2$	78	**5d**: IR (KBr, cm^{-1}) 1732, 1589, 1561, 1446, 1352 1260, 1150
e	$TANH_2$	62	**5e**: IR (KBr, cm^{-1}) 1707, 1592, 1553, 1465, 1370, 1354, 1167

Studies on carbonylation of further imino substrates are in progress in this Laboratory.

Experimental

1.6 g (4.0 mmol) of N-*p*-tosyl-Se,Se-diphenylselenilimine ($4\text{-}CH_3C_6H_4SO_2N{=}SePh_2$) was carbonylated in 10 ml of CH_2Cl_2 in the presence of 50 mg of $PdCl_2(PhCN)_2$ and 0.2 ml of PhCN under 35 bar of CO. The reaction mixture was stirred at RT for 30 min then thermostated at 50 C for 2.5 hours. IR analysis of a diluted portion of the reaction mixture showed an intense band at 2230 cm^{-1}, a typical position for $\nu_{as}NCO$ vibration. The reaction mixture was treated with 0.6 g (4.7 mmol) of 2-chloroaniline (exothermic reaction). The solvent was removed under vacuum and the precipitate was washed with hexane on a glass filter to give 0.83 g of 1-*p*-tosyl-3-(2-chlorophenyl)urea, which corresponds to 64 % yield of the parent tosyl isocyanate.

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