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Catalytic Carbonylation of Nitrobenzene in the Presence of Selenium Compounds

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N-arylcarbamates are extensively used as pesticides. They are commonly synthesized from alcohols and isocyanates, or alternatively from arylamines and chloroformates. Both routes utilize phosgene. Syntheses not involving $COCl_2$ represent considerable interest. We now report high yield procedures based on the carbonylation of nitrobenzene catalyzed by selenium compounds, and show that in the catalytic cycle selenium alternates between the oxidation states zero and 2–.

The carbonylation of aromatic nitrocompounds to N-arylcarbamates

$$ArNO_2 + 3CO + ROH \xrightarrow{\text{catalyst}} ArNHC(O)OR + 2CO_2 \qquad (1)$$

requires noble metals or their compounds [1, 2] as catalysts. Elemental Se and S are also catalytically active [3, 4], but very few data are available on the activity of selenium and sulfur compounds [4, 5].

We have found that the carbonylation of nitrobenzene in ethanol is catalyzed by compounds of selenium, an activator being required in some cases. The results are summarized in Table I.

It is apparent from the Table that the activity of selenium compounds may be comparable with, or higher than that of elemental Se, especially if they are treated with an activator prior to the reaction. The activators applied have the common feature of liberating elemental Se or COSe from the compounds used.

$K_2SeSO_3 \cdot xH_2O$ undergoes proton-assisted decomposition under the reaction conditions [6]:

$$SeSO_3^{2-} + H^+ \rightleftharpoons Se + HSO_3^- \qquad (2)$$

The decomposition of KSeCN is less extensive but can be enhanced by added acetic acid [6]:

$$SeCN^- + H^+ \longrightarrow Se + HCN \qquad (3)$$

Selenourea can liberate Se when reacted with $PhNO_2$, a mild oxidant [7], or react with water present in the reaction mixture:

$$(NH_2)_2CSe + H_2O \longrightarrow 2NH_3 + COSe \qquad (4)$$

TABLE I. Conversion of Nitrobenzene (X) and Selectivity (S) to Ethyl N-phenylcarbamate (EPC) in the Presence of Selenium Compounds as Catalysts. T = 160 °C; 25 bar CO; 3 mmol Se regardless of source; 30 mmol $PhNO_2$; 10 cm^3 Et_3N in 60 cm^3 EtOH; H_2O/Se mole ratio 3.0; reaction time 30 min.

Catalyst	X (%)[a]	S (%)[a]
Elemental Se	89	88
$K_2SeSO_3 \cdot xH_2O$	100	88
KSeCN	28	65
KSeCN[b]	97	95
$(NH_2)_2CSe$	45	95
Ph_3PSe	0	–
Ph_3PSe[c]	100	76
Ph_3PSe[d]	100	95
Ph_3PSe[e]	100	92
$Et_2NC(O)SeMe$	0	–
PhSeSePh	0	–
PhSePh	0	–

[a] Identification of the components and quantitative analyses were carried out by GLC. In some cases TLC and GC-IR were also employed. [b] Treated with 4 mmol acetic acid. [c] Treated with an equivalent amount of 30% aqueous H_2O_2, *cf.* eqn. 5.; H_2O/Se mole ratio 6.0. [d] Same as o, with 70% H_2O_2. [e] Treated with equivalent *m*-chloroperoxybenzoic acid.

Ph_3PSe is completely inactive by itself, but added oxidants lead to excellent conversion and selectivity, owing to the reaction [6]:

$$Ph_3PSe \xrightarrow{O} Se + Ph_3PO \qquad (5)$$

Elemental Se or COSe released in reactions (2)–(5) are the key catalytic species in the carbonylation process. We have previously reported on the effect of water on the catalytic carbonylation [8]. These data permit the conclusion that the catalytic cycle involves the formation of carbonyl selenide, which is hydrolyzed to H_2Se [9] or its salts with Et_3N (water and Et_3N are essential components of all catalyst systems):

$$Se + CO \rightleftharpoons COSe \overset{H_2O}{\rightleftharpoons} H_2Se + CO_2 \qquad (6)$$

$$H_2Se \overset{Et_3N}{\rightleftharpoons} (Et_3NH)(HSe) \overset{Et_3N}{\rightleftharpoons} (Et_3NH)_2Se \qquad (7)$$

The results presented here lead to the conclusion that the catalytic activity of both organic and inorganic selenium compounds can be ascribed to the formation of elemental Se or simple selenium compounds (COSe, H_2Se) capable of participating in the $Se \rightleftharpoons Se^{2-}$ catalytic cycle. Thus various selenium compounds may exhibit various catalytic activities

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owing to their different degrees of decomposition.

The exact mechanism of this complex catalytic reaction cannot be established at present. The possible involvement of phenylnitrene as intermediate has been suggested [2, 10]. We carried out the reaction using nitrosobenzene as starting material instead of $PhNO_2$ and in the early stages of the process detected considerable amounts of azoxybenzene. Its formation can be readily interpreted in terms of the reactions:

$$PhNO + H_2Se \longrightarrow PhN + H_2O + Se \qquad (8)$$

$$PhNO + PhN \longrightarrow PhN(O)NPh \qquad (9)$$

The formation of phenylnitrene can also be expected in the case of nitrobenzene reduction. Work is in progress on further mechanistic aspects of these carbonylations.

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