

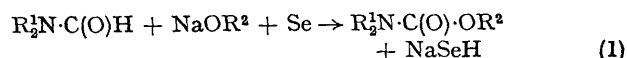
An Unusual Oxidation of the Formyl Hydrogen Atom of Formamides by Selenium

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Summary Elemental selenium was found to oxidise the formyl hydrogen atom of dimethylformamide in the presence of alkoxide to give alkyl *NN*-dimethylcarbamate under mild conditions.

We report that elemental selenium acts as a novel oxidising agent^{1,2} for *NN*-dimethylformamide (DMF) in the presence of sodium alkoxide to give alkyl *NN*-dimethylcarbamate and sodium hydrogen selenide at room temperature [reaction (1), (Table)]. This reaction involves a unique oxidation of formyl hydrogen by Se followed by substitution with alkoxy-anion. Formation of the carbamate was not observed when DMF and sodium alkoxide were allowed to react under similar conditions in the absence of Se.



Addition of methyl iodide[§] to the reaction mixture of DMF, Se, and sodium ethoxide gave $\text{Me}_2\text{N}\cdot\text{C}(\text{O})\cdot\text{SeMe}$, showing the presence of $\text{Me}_2\text{N}\cdot\text{C}(\text{O})\cdot\text{SeH}$,³ which was then

TABLE. Selenium oxidation^a of $\text{R}^1\text{R}^2\text{N}\cdot\text{C}(\text{O})\text{H}$ in the presence of R^3ONa

$\text{R}^1\text{R}^2\text{N}$	R^3	$\text{R}^1\text{R}^2\text{N}\cdot\text{C}(\text{O})\cdot\text{OR}^3$ Yield (%) ^b
Me_2N	Me	36
Me_2N	Et	35
Me_2N	Bu ⁿ	24
Me_2N	Bu ^t	15
Me_2N	Ph	0
Et_2N	Et	14
MeNH	Et	13
NH_2	Et	4
PhNH	Et	0

^a Formamide (0.1 mol), NaOR^3 (0.01 mol), and metallic Se (1 mg atom) in 20 ml THF, at room temperature under N_2 for 20 h. ^b From g.l.c. in comparison with an authentic sample.

attacked on the carbonyl carbon by alkoxide anion to give the carbamate. Formation of sodium hydrogen selenide⁴ was confirmed by the addition of an alkylating agent followed by oxidation with oxygen to yield dialkyl diselenide.[¶]

(Received, 12th November 1973; Com. 1550.)

[§] No *NN*-dimethylacetamide could be detected whose presence would suggest an intermediacy of *NN*-dimethylcarbamoyl anion.

[¶] From g.l.c. and mass spectrometry.

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³ K. Kondo, N. Sonoda, and S. Tsutsumi, *Chemistry Letters*, 1972, 373, 401.

⁴ D. L. Klayman and J. S. Griffin, *J. Amer. Chem. Soc.*, 1973, **95**, 197.