A New Hydrogen Selenide–Triethylamine Catalysed Synthesis of Formanilides from Aromatic Amines and Carbon Monoxide

By KIYOSHI KONDO,* NOBORU SONODA,† and HIROSHI SAKURAI

(*The Institute of Scientific and Industrial Research, Osaka University and* †*Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka,* 565, *Japan*)

Summary The triethylamine salt of hydrogen selenide is an effective catalyst in the synthesis of formanilides by the reaction of aromatic amines with carbon monoxide under pressure.

THERE have been several reports[1] on catalytic formylation of amines with carbon monoxide. We have found that the triethylamine salt of hydrogen selenide effectively catalysed the reaction of aromatic amines with carbon monoxide [reaction (1)].

$$ArNH_2 + CO \xrightarrow{Et_3N \cdot H_2Se} ArNHCHO \qquad (1)$$

In a typical reaction, aniline (38·2 g), and $Et_3N \cdot H_2Se$[2] (0·01 mol) were heated at 100° under 50 kg cm^{-2} CO for 45 h followed by oxidation with oxygen at room temperature to give formanilide (3·8 g, 3·1 g equiv. per g equiv. catalyst).‡ Additional reaction time, higher pressure of CO, and higher temperature increased the yield of formanilide. In the absence of the catalyst formanilide was not formed.

The catalyst could be prepared *in situ* by reaction (2).[3]§

$$2\,ArNH_2 + CO + Se + Et_3N \rightarrow (ArNH)_2CO + Et_3N \cdot H_2Se \qquad (2)$$

The catalyst prepared in this way exhibited the same activity as the pure salt. The results obtained from several aryl amines using the catalyst generated *in situ* are summarized in the Table.

TABLE. Relative reactivity[a] of aromatic amines

$X\text{-}C_6H_4NH_2$ X	$X\text{-}C_6H_4NHCHO$ k_X/k_H[b]
H	1·0
p-Me_2N	6·5
p-MeO	2·35
p-Me	1·91
m-Me	1·20
o-Me	0·39
p-Cl	0·49
p-Br	0·48

[a] RNH_2 (0·04 mol), Et_3N (50 ml), H_2Se (0·001 mol) and CO 50 kg/cm^2, 180°, 7 h. [b] From g.l.c.

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‡ Trace amounts of 1,3-diphenylurea were formed due to the fast reaction [reaction (2)] of CO in solution with atomic selenium generated by oxidation of hydrogen selenide.

§ No formanilide was produced after reflux in triethylamine under CO (1 atmos.).

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