High-Pressure Preparation of Carbanilide from Nitrobenzene, Carbonyl Sulfide, Carbon Monoxide, and Water

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Carbanilide is prepared from nitrobenzene in a procedure which requires only one process step. An aromatic nitro compound is treated with a mixture of carbonyl sulfide, carbon monoxide, and water in an organic base such as pyridine. Yields of 50 mol % of carbanilide from nitrobenzene are obtained. Aniline, a reaction intermediate, is the only other major product. A German patent, 2,317,122, has recently shown that this process can be extended to the preparation of *N*-aryl-*N'*-alkyl ureas starting with an aryl nitro compound and an alkyl amine.

This report describes a procedure which requires only one process step for the conversion of nitrobenzene to carbanilide in which only nitrobenzene, carbon monoxide, and water are consumed. The pathway proposed for this process is shown in Scheme 1. Carbonyl sulfide is hydrolyzed to give hydrogen sulfide and carbon dioxide (*9*). The hydrogen sulfide reduces the nitrobenzene to aniline with sulfur as a by-product (*2, 6, 7*). The sulfur reacts with carbon monoxide to give carbonyl sulfide (*10*). The aniline reacts with carbonyl sulfide to form carbanilide (*1, 4*). Although sulfur compounds are involved in each step of the reaction, they are neither produced nor consumed in the net reaction.

Scheme 1

$$5COS + 5H_2O \rightarrow 5H_2S + 5CO_2 \tag{1}$$

$$2\phi NO_2 + 6H_2S \rightarrow 2\phi NH_2 + 4H_2O + 6S^\circ \tag{2}$$

$$6S^\circ + 6CO \rightarrow 6COS \tag{3}$$

$$2\phi NH_2 + COS \rightarrow (\phi NH)_2CO + H_2S \tag{4}$$

Net reaction:

$$2\phi NO_2 + 6CO + H_2O \rightarrow (\phi NH)_2CO + 5CO_2 \tag{5}$$

Hydrolysis of carbonyl sulfide and hydrolysis of carbanilide are competing reactions. Limiting the water concentration in the reaction mixture by staged addition of water increases the yield of carbanilide.

Aniline is a by-product. By lowering the concentration of carbonyl sulfide, it is possible to produce aniline exclusively, again consuming only carbon monoxide and water. Other procedures exist for the reduction of nitrobenzene to aniline with carbon monoxide (*8*).

While this work was in progress, a similar procedure was reported for the preparation of *N*-aryl-*N'*-alkyl ureas. Preparation of *N,N'*-diaryl ureas was not mentioned in this patent (*5*), and other literature (*4*) indicates that *N,N'*-diaryl ureas are prepared in very poor yields from the reaction of aryl amines with carbonyl sulfide. The procedure now described is unique in that the staged addition of water allows the formation of these ureas in acceptable yields from reactions of carbonyl sulfide. Recently, Dieck et al. (*3*) reported a low-pressure process for carrying out similar transformations on nitro aromatics, but these reactions required the use of noble metals in soluble form.

Experimental

Carbanilide preparation. Nitrobenzene (100 g, 0.83 mol), pyridine (75 g), and carbonyl sulfide (168 g, 2.8 mol) were charged to a liter autoclave. Carbon monoxide was added to 1000 psig. A mixture of water (7.3 g, 0.405 mol) and pyridine (50 ml) was pumped into the autoclave over an hour, and the temperature was maintained at 200 °C for an additional hour. After the autoclave cooled, the contents were treated with pyridine (500 ml) to dissolve the carbanilide. The total reactor effluent was analyzed by combined GC and mass spectrometry (column: 4-ft × ⅛-in. SS; 10% polyphenylether (6-ring) on 40–60 Chromosorb T; program 80–180 °C @ 6 °C/min, flame detector). Carbanilide could not be determined by GC because it decomposed to aniline and phenyl isocyanate in the entrance port. It was therefore determined by liquid chromatography (column: 0.5 M × 0.26 cm packed with ether permaphase (Du Pont); mobile phase: 1.5 ml/min flow of 3% THF in isooctane; detector: UV absorption at 254 nm).

Conversion of nitrobenzene was 86%. Selectivity was 65% carbanilide, 35% aniline, and a trace of thiocarbanilide. Material balance was 97 mol %.

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