

A New Selenium-Triethylamine Catalysed Synthesis of Arylureas from Carbon Monoxide and Aromatic Amines

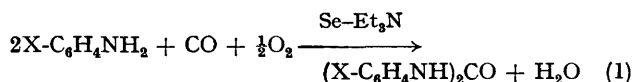
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Summary Arylureas have been synthesized conveniently using selenium and triethylamine as co-catalyst under mild conditions by the reaction of carbon monoxide with aromatic amines

We have shown that carbon monoxide reacts with ammonia or aliphatic amines in the presence of selenium under mild conditions to form urea or its derivatives.¹ However, aromatic amines failed to react under the conditions in which the aliphatic ureas were formed stoichiometrically.

Recently, we found that strongly basic tertiary amines such as triethylamine can be successfully used as a co-catalyst and we now report a novel method for the preparation of symmetrical diarylureas [reaction (1)].



In a typical reaction, aniline (3.72 g, 0.04 mol) and triethylamine (2.02 g, 0.02 mol) were added to 50 ml of benzene, and the solution heated under reflux at 80 °C under CO, for removal of dissolved O₂. Amorphous selenium† (0.0789 g, 0.001 g atom) was added with cooling, and carbon monoxide was blown into the solution under atmospheric pressure at room temperature at a rate of 60 ml per min until the selenium was completely dissolved. Thereafter, oxygen was passed in at a rate of 0.4 ml per min, together with carbon monoxide, for 4 h. The flow of carbon monoxide was then stopped but the flow of oxygen was continued to precipitate selenium. Removal of the recovered selenium and the solvent left 0.953 g of 1,3-diphenylurea which corresponded to 4.58 g equivalent per g equivalent of the selenium used. 1,3-Diphenylurea was formed in stoichiometric yield, based on selenium used,

when the passage of CO and O₂ was omitted from the procedure. The results obtained from several aryl amines are summarized in the Table.

Synthesis^a of diarylureas from aromatic amines

X-C ₆ H ₄ NH ₂	Catalytic reaction time ^b (h)	(X-C ₆ H ₄ NH) ₂ CO Yield (%) ^c
X		
<i>p</i> -MeO	4	41.1
<i>p</i> -Me	4	37.0
<i>m</i> -Me	4	26.3
<i>o</i> -Me	4	16.0
H	4	22.9 ^d
H	10	59.0
<i>p</i> -NH ₂	4	24.0
<i>p</i> -Cl	4	18.5

^a Aromatic amine (0.04 mol), triethylamine (0.02 mol), and amorphous selenium (0.001 g atom) were treated with carbon monoxide in 50 ml of benzene, and the procedure was almost identical to that described for the representative example. ^b The time for the reaction of mixture gas of CO and O₂. ^c Yields (%) based on aromatic amine used. Each yield was quantitative to the aromatic amine changed, and the unchanged aromatic amine was recovered. ^d This corresponds to 4.58g equivalent per g equivalent of the selenium used.

Additional reaction time caused an increase in the yield of ureas. In the absence of triethylamine, the selenium was not dissolved, and the reaction therefore did not proceed.

(Received, 2nd December 1971; Com. 2061.)

† Metallic selenium can also be used, but dissolution of selenium took longer.

¹ N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda, and S. Tsutsumi, *J. Amer. Chem. Soc.*, 1971, **93**, 6344.