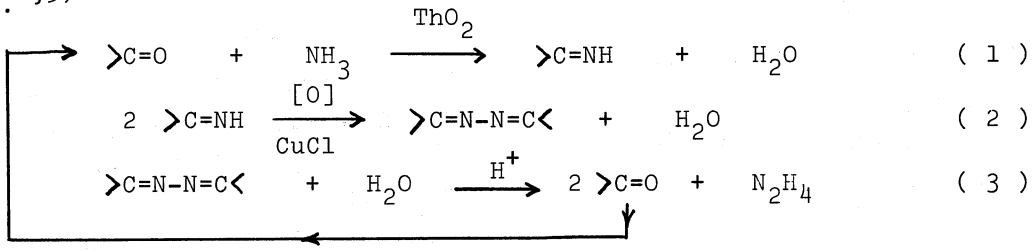
CHEMISTRY LETTERS, pp. 89-90, 1974. Published by the Chemical Society of Japan

A LIQUID-PHASE ONE-STAGE PROCESS FOR KETAZINE SYNTHESIS DIRECTLY FROM BENZOPHENONE, AMMONIA AND OXYGEN IN THE PRESENCE OF $ZnCl_2$ AND CuCl[1)]

Hiromu HAYASHI, Kengo KAWASAKI, and Tsutomu MURATA
Department of Chemical Engineering, Tokushima University
Minamijosanjima, Tokushima 770

A new procedure for the synthesis of benzophenone azine is described. An equi-molar mixture of NH_3 and O_2 was passed through benzophenone in the presence of $ZnCl_2$ and CuCl at 200°C to obtain benzophenone azine in good yield.

Benzophenone azine, which gives hydrazine quantitatively by acid hydrolysis,[2)] is prepared by the oxidative coupling of diphenylmethanimine in the presence of cuprous chloride.[3,4)] Benzophenone reacts selectively with ammonia to form diphenylmethanimine over thoria.[5)] A process for hydrazine synthesis via ketazine will be possible.[4,5)]



It is of interesting to prepare ketimine in the liquid phase, as the synthesis of ketazine directly from ketone, ammonia and oxygen will be achieved "in a single reactor" combining stages (1) and (2).

In the present study, it has been found that zinc chloride is an effective catalyst for stage (1) as shown in Fig. 1. An equi-molar mixture of ammonia and nitrogen was passed through 18.2g of benzophenone at a rate of 2 ℓ/hr at 200°C to form diphenylmethanimine. Two series of runs were made with different amounts of zinc chloride, the one 0.3g and the other 1.0g. The former was homogeneous while in the latter some of the zinc chloride added precipitated at the reaction condition. No

diference on the rate of ketimine formation were observed in these two series.

The authors successfully tried to obtain benzophenone azine directly from benzophenone, ammonia and oxygen, as shown in Fig. 2, by the "in situ" oxidative coupling of diphenylmethanimine. In the above mentioned procedure for ketimine synthesis, nitrogen was replaced by oxygen and cuprous chloride was added with zinc chloride. It is noteworthy that the yield of benzophenone azine in the direct synthesis (Fig. 2) is better than that of expected from the ketimine synthesis (Fig. 1). The isolation of ketimine is unnecessary for the purpose of ketazine synthesis, and the direct method would be promising for industrial process.

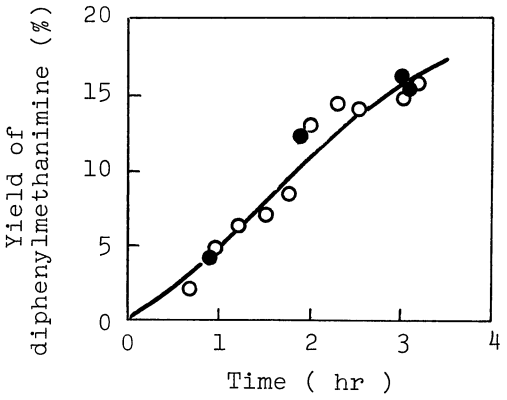


Fig. 1 Formation of diphenylmethanimine via dehydrative condensation of benzophenone with ammonia in the presence of $ZnCl_2$

Temp. 200°C, $Ph_2C=O$ 18.2g
Flow rate (50%NH_3,50%N_2) 2 l/hr
$ZnCl_2$ o ; 0.3g, ● ; 1.0g

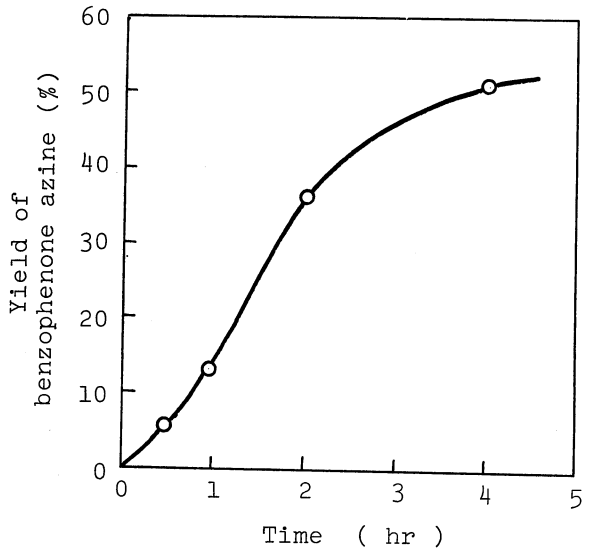


Fig. 2 Synthesis of benzophenone azine directly from bezophenone, ammonia and oxygen in the presence of $ZnCl_2$ and CuCl

Temp. 200°C, $Ph_2C=O$ 18.2g
Flow rate (50%NH_3,50%O_2) 2 l/hr
$ZnCl_2$ 0.3g, CuCl 0.5g

References

1) "Reaction Engineering Studies on Ammonia-Hydrazine Conversion Processes. IV "
2) R.Meyer, Brit.P.,843,587(Aug.4,1960).
3) H.Hayashi, H.Nishi and K.Kawasaki, Nippon Kagaku Kaishi, 1973, 1949.
4) R.Meyer and D.Pillon, U.S.P.,2,870,206(Jan.20,1959).
5) H.Hayashi, H.Nishi and T.Abe, Nippon Kagaku Kaishi, 1973, 1392.

(Received December 10, 1973)