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NH_4Cl-CuCl AS A CATALYST FOR THE SYNTHESIS OF KETAZINE DIRECTLY FROM BENZOPHENONE, AMMONIA AND OXYGEN$^{1)}$

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A new catalyst, NH_4Cl-CuCl, for the synthesis of benzophenone azine is proposed. The recovery of expensive CuCl should be simplified than in the case of $ZnCl_2$-CuCl.$^{2)}$ An improved catalyst, NH_4Cl-CuCl·Ph_2C=NH, is also descrived.

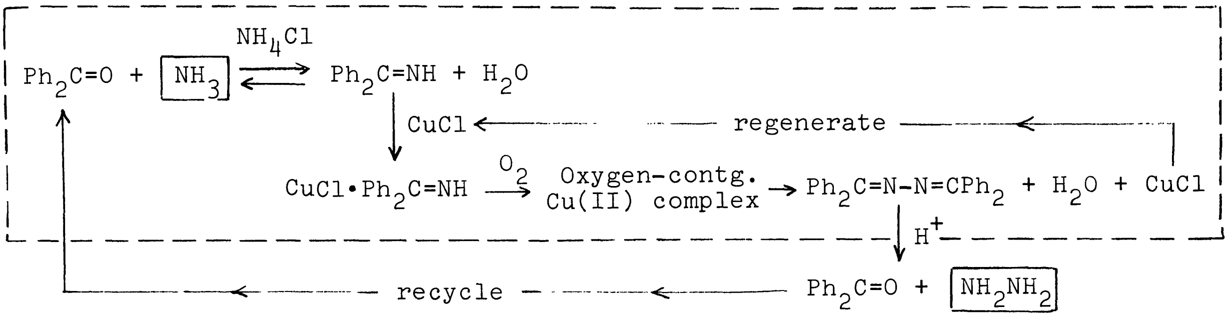
A liquid-phase process for the synthesis of benzophenone azine directly from benzophenone, ammonia and oxygen in the presence of $ZnCl_2$ and CuCl has been proposed in the previous paper.$^{2)}$ The separation of catalyst to recover expensive CuCl is an important problem for the direct method to develop as an industrial process. Meyer and Pillon of Rhône-Poulenc claim in their patent$^{3)}$ to use aquous NH_4Cl for the separation of CuCl in the oxidative coupling of diphenylmethanimine. The dehydrative condensation of benzophenone with ammonia is acid-catalyzed reaction. And if NH_4Cl, which is weakly acidic, catalyzes the formation of ketimine, the recovery of CuCl will be simplified.

The expected results were obtained 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 in the presence of NH_4Cl. Diphenylmethanimine is easily hydrolyzed without the continuous removal of water by heating the exaust-lines up to about 250°C.

The catalyst was applied for the direct synthesis of benzophenone azine as shown in Fig. 2. In the above mentioned procedure for ketimine synthesis, nitrogen was replaced by oxygen and CuCl was added with NH_4Cl. Diphenylmethanimine is successively converted into ketazine by the "in situ" oxidative coupling without isolation. And thus, benzophenone azine is prepared in a single reactor starting from benzophenone. As is observed in the case of $ZnCl_2$-CuCl,$^{2)}$ the yield of ketazine in Fig.2 is better than that of expected from the apparent rate of formation of ketimine (Fig.1). The results are nothing curious: the formation of ketimine is reversible, and thus the oxidative coupling of ketimine itself has the same effect of the removal of water. Fortunately, benzophenone azine is rather stable for hydrolysis. As the oxidation is fast enough, none of ketimine were detected at a condition given in Fig. 2.

It is inevitable for the direct method that the yield-time curves are S-shaped as a result of the absence of ketimine at the initial stage of the reaction. In the oxidative coupling of diphenylmethanimine, a copper-ketimine complex, CuCl·Ph_2C=NH, is formed as intermediate, which is converted into ketazine via an oxygen-containing copper(II) complex.$^{4)}$ The oxidation proceeds by the catalytic amounts of CuCl in the presence of excess ketimine. The regenerated CuCl repeatedly forms CuCl·Ph_2C=NH. The formation of ketazine will be delayed in the direct process untill the effective amounts of the intermediate complex are formed. It should be profitable to use $NH_4Cl\text{-}CuCl \cdot Ph_2C{=}NH$ as a catalyst in place of $NH_4Cl\text{-}CuCl$. The presumption was confirmed that the induction period was diminished as shown in Fig. 2.

Benzophenone azine quantitatively gives hydrazine by acid-hydrolysis.$^{5)}$ A continuous process for hydrazine synthesis from ammonia will be possible by recycling benzophenone as shown in the following scheme, where the reactions closed by dashed-lines are carried out in a single reactor.



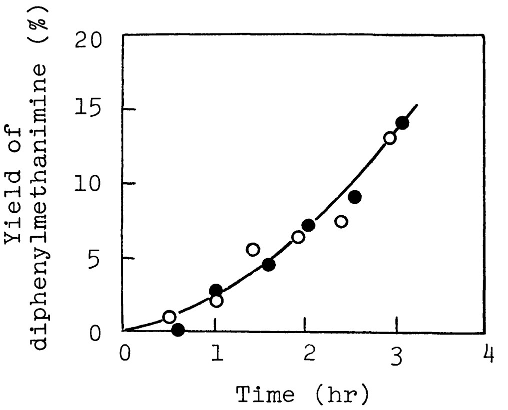


Fig. 1. Dehydrative condensation of benzophenone with ammonia in the presence of NH_4Cl.

Temp. 200°C, $Ph_2C{=}O$: 18.2g,

Flow rate (50% NH_3, 50% N_2): 2 ℓ/hr

NH_4Cl: ○ ; 0.5g, ● ; 1.0g

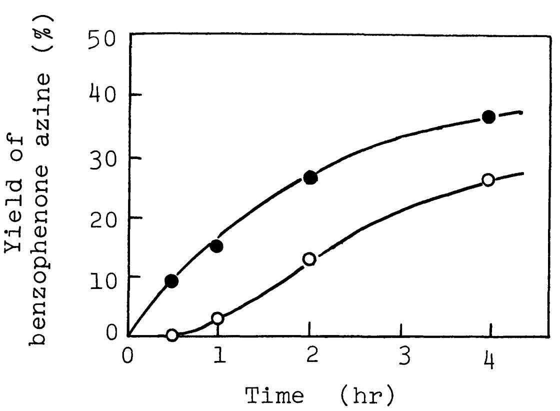


Fig. 2. Synthesis of benzophenone azine directly from benzophenone, ammonia and oxygen in the presence of $NH_4Cl\text{-}CuCl$ and $NH_4Cl\text{-}CuCl \cdot Ph_2C{=}NH$.

Temp. 200°C, $Ph_2C{=}O$: 18.2g, NH_4Cl: 0.5g,

Flow rate (50% NH_3, 50% O_2): 2 ℓ/hr

○ : CuCl 0.5g, ● : $CuCl \cdot Ph_2C{=}NH$ 1.4g

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