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DEHYDRATIVE CONDENSATION OF BENZOPHENONE WITH AMMONIA CATALYZED BY ION-EXCHANGE RESINS AND ITS APPLICATION TO AZINE SYNTHESIS1)2)

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Diphenylmethanimine was selectively formed by passing ammonia through benzophenone at 200°C in the presence of ion-exchange resins. Attempts were made to obtain azine directly from benzophenone, ammonia and oxygen using the resins with CuCl and revealed acidic resins to be active while basic ones less active.

The aerial oxidation process3 for hydrazine synthesis involves (1) the dehydrative condensation of benzophenone with ammonia to diphenylmethanimine and (2) the subsequent oxidation of the imine to benzophenone azine. Thoria4) and thoria-silica5) are suitable for step(1) in a gas-phase, zinc chloride6) and ammonium chloride7) also for (1) in a liquid-phase, and cuprous chloride8) for (2) in a liquid-phase. It is, however, troublesome in the homogeneous catalysis to recover the catalysts for recycle use.9) A possibility to simplify the catalyst separation may be found by employing *fixed-catalyst*, which is suitable for irrigated packed column reactor. Step(1) is an acid-base catalyzed reaction and it seemed likely that ion-exchange resins might be favorable for the present purpose.

Ion-exchange resins used are listed in Table 1. Acidic and basic resins were treated with 8% HCl and 5% NaOH, respectively, washed and dried in air and finally under a vacuum at 120°C.

An equimolar mixture of ammonia and nitrogen was passed through 18.2g of benzophenone in the presence of 3g of an ion-exchange resin at 200°C under atmospheric pressure at a rate of 2 l/hr for 3 hr. Diphenylmathanimine was selectively formed and the activities of the six resins were nearly the same order as shown in Table 1. It was previously shown2,6-8) that azine could be obtained directly from benzophenone,

Table 1. Dehydrative condensation of benzophenone with ammonia in the presence of ion-exchange resins.
$Ph_2C=O$ 18.2g, Resin 3g, 200°C, $NH_3/N_2=1/1$, 2 l/hr, 3 hr

Ion-exchange resin		Diphenylmethanimine imine Yield(%)
Amberite IR-120B	(SA)	11.2
200C	(SA,MR)	12.1
IRC-50	(WA,MR)	7.1
IRA-900	(SB)	13.2
IRA-400	(SB,MR)	8.5
IRA-93	(WB,MR)	9.3

S:strongly, W:weakly, A:acidic, B:basic, MR:macroreticular

Table 2. Direct synthesis of azine from benzophenone, ammonia and oxygen using ion-exchange resins with CuCl.
$Ph_2C=O$ 18.2g, Resin 3g, CuCl 0.5g, 200°C, $NH_3/O_2=1/1$, 2 l/hr, 3 hr

Resin	Yield (%)	
	Imine	Azine
IR-120B	3.0	24.5
200C	0	22.0
IRC-50	0	12.6
IRA-900	4.7	0.9
IRA-400	4.0	2.6
IRA-93	0	16.0

ammonia and oxygen, combining the catalysts for steps(1) and (2), where the intermediate product imine undergoes *in situ* oxidative coupling. Thus the ion-exchange resins as the catalyst for step(1) were applied for the direct synthesis of azine. Nitrogen was replaced by oxygen in the procedure described above, and cuprous chloride was added with an ion-exchange resin. It was found that acidic resins were active while basic ones less active as shown in Table 2. The activities of strongly acidic resins-CuCl are comparable with that of NH_4Cl-CuCl$^{7)}$, promising for industrial use.

References

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