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SELECTIVE MONOBROMINATION OF ANILINE DERIVATIVES BY USE OF BROMINE ADSORBED ON ZEOLITE 5A

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Aniline is selectively brominated by use of molecular bromine adsorbed on zeolite 5A in carbon tetrachloride to give monobromoanilines. Coexistence of organic bases such as pyridine and 2,6-lutidine increases the yield and selectivity of 4-bromoaniline. o-, m-, and p-Toluidines are also monobrominated selectively according to the present procedure.

Recently several monobromination reagents for reactive aromatic amines such as aniline have been developed; e.g. 2,4,4,6-tetrabromocyclohexa-2,5-dienone,[1] N-bromosuccinimide-dimethylformamide,[2] hexabromocyclopentadiene.[3] Indirect selective bromination of aniline has also been reported to proceed by the reaction of aniline hydrobromide salt with dimethyl sulfoxide[4] or by the reaction of anilinosilane with N-bromosuccinimide.[5] Molecular bromine is too reactive to induce selective bromination, but the combined use of bromine and zeolite has been reported to be applicable to the selective bromination of halobenzenes and alkylbenzenes.[6,7] This method, however, has not been successfully applied to the selective bromination of the aromatic compounds with highly activating groups.[6] Here we report that bromine pre-adsorbed on zeolite 5A can monobrominate aniline and its derivatives with high selectivity in the presence of pyridine or 2,6-lutidine.

Aniline was treated with the bromine adsorbed on various types of zeolite in CCl_4 (Table 1). Zeolite 5A showed the highest selectivity (92%) for the monobromination.[8] The pre-adsorption of bromine on 5A was requisite for the selective bromination since the addition of bromine to aniline adsorbed on 5A in CCl_4 caused nonselective bromination.

Coexistence of organic bases such as pyridine and 2,6-lutidine not only improved the aniline conversion owing to neutralization of the generated HBr but also increased the para-bromination selectivity.

A typical experimental procedure is as follows: Powdered zeolite 5A (3 g), dried at 400 °C for 3 h, was stirred in a CCl_4 solution (10 ml) of bromine (1.05 mmol) at room temperature for 2 h. To the resulting mixture was added a CCl_4 solution (2 ml) of aniline (1.0 mmol) and organic base (2.0 mmol) at 0 °C, and stirring was continued at room temperature for 20 h. Aqueous sodium thiosulfate was then added, and the resulting mixture was made alkaline, filtered, and

Table 1. Bromination of aniline with bromine adsorbed on various zeolites

Zeolite	Base	Aniline conversion / %	Product selectivity / % 4-[a]	2-[b]	2,4-[c]	2,4,6-[d]
None	—	60	33	0	57	10
13X	—	41	60	14	11	14
13Y	—	62	75	7	10	9
Mordenite	—	21	67	17	10	5
3A	—	69	64	0	19	17
4A	—	67	65	2	27	5
5A	—	63	75	17	7	0
5A	Pyridine	81	91	8	< 1	0
5A	2,6-Lutidine	84	93	7	< 1	0

a) 4-Bromoaniline. b) 2-Bromoaniline. c) 2,4-Dibromoaniline. d) 2,4,6-Tribromoaniline.

extracted with CH_2Cl_2. The products were analyzed by means of GLC.

The combined use of bromine adsorbed on 5A and 2,6-lutidine also induced the monobromination of o-, m-, and p-toluidines to give 4-bromo-2-methylaniline, 4-bromo-3-methylaniline, and 2-bromo-4-methylaniline, respectively, in over 94% selectivity.

The present method, which requires only easily available reagents (bromine, zeolite 5A, and organic base) and can be operated under mild reaction conditions, appears to be useful for the selective bromination of aromatic amines.

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