Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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N. Narender [a] , P. Srinivasu [a] , S. J. Kulkarni [a] & K. V. Raghavan [a]

[a] Catalysis Group, Indian Institute of Chemical Technology , Hyderabad, 500 007, India

To cite this article: N. Narender , P. Srinivasu , S. J. Kulkarni & K. V. Raghavan (2000) Liquid Phase Regioselective Bromination of Aromatic Compounds Over Hzsm-5 Catalyst, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:20, 3669-3675, DOI: 10.1080/00397910008086993

To link to this article: http://dx.doi.org/10.1080/00397910008086993

SYNTHETIC COMMUNICATIONS, 30(20), 3669–3675 (2000)

LIQUID PHASE REGIOSELECTIVE BROMINATION OF AROMATIC COMPOUNDS OVER HZSM-5 CATALYST

N. Narender, P. Srinivasu, S. J. Kulkarni* and K. V. Raghavan

Catalysis Group, Indian Institute of Chemical Technology, Hyderabad – 500 007, India

Abstract: A simple, efficient, regioselective and environmentally safe method for oxybromination of activated aromatics catalyzed by HZSM-5 is reported. The electrophilic substitution of bromine generated from KBr using HZSM-5 as a catalyst and H_2O_2 as an oxidant.

Use of heterogeneous catalysts such as clays and zeolites in organic synthesis has received considerable attention in the past few years, mainly due to the minimum production of byproducts and pollutant materials[1-5]. In fact, the possibility of performing efficient chemical transformations with reusable catalysts avoiding toxic reagents, large amount of solvents, and expensive purification methods represents a fundamental target of the modern organic synthesis.

Brominated arenes are versatile intermediates in the synthesis of wide variety of biologically active compounds. Consequently, a variety of methods for

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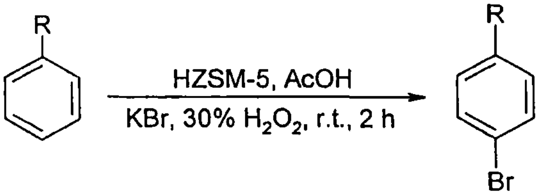
IICT Communication No.; 4364

*To whom correspondence should be addressed
Fax : 0091 – 40 – 7173387 / 7173757; E – mail : sjkulkarni@iict.ap.nic.in

the bromination of aromatics have been reported in the literature ranging from Br_2-Lewis acids, N-bromosuccinamide(NBS)-H_2SO_4, NBS-SiO_2, NBS-PTSA, Br_2-zeolite, NBS-zeolite, KBr-Ammonium molybdate, NBS-Amberlyst, NBS-NaOH, NBS-$HBF_4.Et_2O$[6-15]

The classical direct bromination of aromatic systems suffers from being wasteful in the bromine employed. One half ends up as hydrogen bromide. In large-scale operations this is an environmental as well as an economic problem. In oxybromination, HBr is being used as a bromine source, H_2O_2 as an oxidant[16,17]. Which was thought to be possible solution to overcome these difficulties met with partial success, since HBr is highly toxic and corrosive and is as harmful as molecular bromine to the environment. We have designed a novel heterogeneous catalytic system to generate electrophilic bromine *in situ* from easily available KBr, H_2O_2 as an oxidant for the oxybromination as a possible alternative to solve the disadvantages described in the earlier methods. Herein we report a new method for the para selective oxybromination of activated aromatics using shape selective zeolite (HZSM-5) as a catalyst, H_2O_2 as an oxidant and KBr as a bromine source.



Scheme

The results are summarized in Table 1. These systems yield selectively para brominated aromatics unless the para-position (entry 11) is substituted . The

Table 1. HZSM-5 catalysed regioselective oxybromination of activated aromatic compounds

Entry	Substrate	t/h	Conversion (%)	Yield[a](%) Para	Ortho
1.1	Anisole	2	99	98	-
1.2	Anisole[b]	2	43	43	-
1.3	Anisole[c]	2	44	44	-
1.4	Anisole[d]	2	0	-	-
1.5	Anisole[e]	2	32	32	-
1.6	Anisole[f]	2	0	-	-
2	Acetanilide	2	99	98	-
3	Aniline	4	91	76	15
4	N, N-Dimethylaniline	4	95	92	3
5	2-Nitroaniline	4	93	77	15
6	2-Aminobenzonitrile	4	79	50	28
7	o-Toluedine	4	97	81	15
8	o-Anisidine	4	81	60	9
9	2, 6-Dichloroaniline	4	98	95	-
10	o-Bromoaniline	4	99	67	29
11	p-Cresol	4	95	-	70

a). The products were characterised by NMR, Mass, GC analysis

b). HY was used as catalyst, c). SiO_2-Al_2O_3 used as catalyst

d). Reaction was carried out in absence of H_2O_2

e). Reaction was carried out in absence of catalyst

f). Reaction was carried out in absence of catalyst and H_2O_2

para-substituted aromatics were brominated in the ortho-position. The yields were generally good to excellent. The reaction is slow with para selectivity when conducted in the absence of catalyst.

Inspite of the presence of electron-withdrawing substituents such as cyano and a nitro group (entries 5&6), regiospecific bromination in good yields have been observed. When the less reactive aromatics such as toluene, bromobenzene, however, failed to undergo bromination under the same reaction conditions.

A wide range of solvents have been employed in these reactions including, CH_3CN, CH_2Cl_2, CCl_4. The best results were obtained when acetic acid was used as a solvent compared to others. The para selectivity may be explained in terms of reactions occurring inside the cavity of the zeolite. The catalyst was highly crystalline before and after the reaction. There was no leaching of aluminum from the zeolitic framework.

The brominated aromatic products were analyzed by GC and isolated products were also analyzed by ^{1}H NMR, and Mass spectroscopy.

In conclusion we developed an efficient new method for the oxybromination of activated aromatics. The present catalytic method which is more attractive than the earlier methods, offers the additional advantages such as mild conditions, high yield, economical, easy set-up and work-up, selective monobromination with high para selectivity, inexpensive and environmentally friendly catalysts.

Experimental

HZSM-5(30) was obtained from Conteka, Sweden. The SiO_2/Al_2O_3 ratio was 30 and surface area ~ 400 $m^2.g^{-1}$.

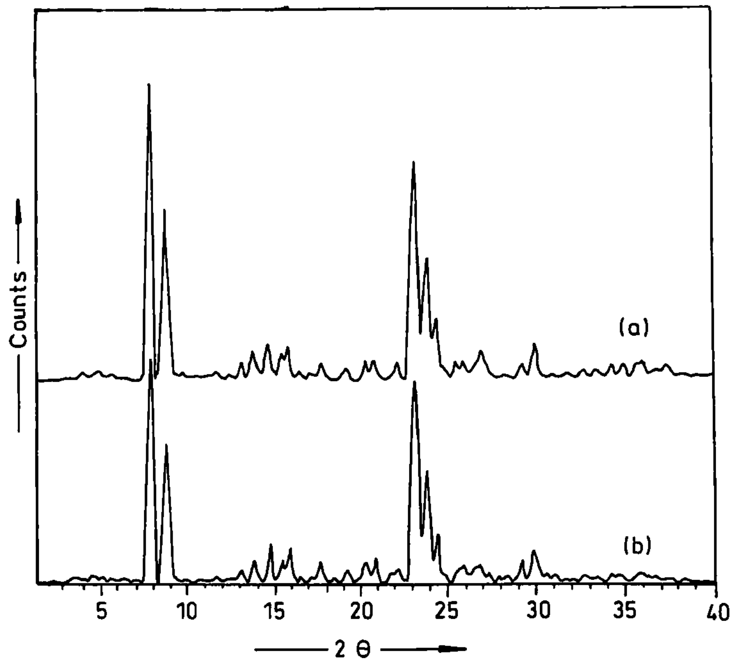


Fig.1 XRD pattern of a) HZSM-5 (before reaction) b) HZSM-5 (after reaction)

General procedure for the bromination of aromatic compounds

A 50 ml two necked round bottomed flask was charged with 200 mg of zeolite, the substrate (2 mmol) and KBr (2.2 mmol) in acetic acid (4 ml). 30% H_2O_2 (2.2 mmol) was then, added dropwise to the reaction mixture and the contents allowed to stir at room temperature. The reaction was monitered by thin layer chromatography (TLC). After the completion of the reaction, the catalyst was filtered and the solid was washed with ether. The combined filtrates were washed with saturated sodium bicarbonate solution. The organic extract was dried over anhydrous sodium sulfate and solvent evaporated under reduced pressure.

The products were purified by column chromatography and confirmed by ^{1}H NMR Mass spectra.

Acknowledgements

We are thankful to Department of Science &Technology, New Delhi for funding, DST Project No. : SP/S1/H07/97.

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Received in the UK 9/1/99