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Selectivity in Bromination of Alkylbenzenes in the presence of Montmorillonite Clay

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*Abstract:*Bromination of alkylbenzenes using bromine in carbon tetrachloride yields ring brominated products in the presence of K10-montmorillonite. In contrast, bromination without clay results only in side-chain bromination.

INTRODUCTION

Clays and clay-based reagents find extensive applications in organic synthesis.[1-4] Cation-exchanged montmorillonite clays are used as efficient solid acid catalysts and clay-supported reagents find wide range of applications from catalysis to molecular devices. Clay - directed aromatic substitutions such as nitration[5,6], Friedel-Craft's acylation[7] and alkylation[8] were reported extensively. Pillared clays are also extensively employed for selective organic transformations[9,10] and find industrial applications in areas which are hitherto dominated by zeolites. Our interest[11,12] in utilising clays for achieving selectivity and catalysis in organic reactions prompted us to investigate bromination of alkylbenzenes in clay microenvironment.

Side-chain bromination of aromatic hydrocarbons (aryl alkyl systems) is favoured by "radical conditions" (presence of light, peroxide and/or nonpolar solvents), while "ionic conditions" such as polar solvents, metals, Friedel-Craft's catalysts[13] favour electrophilic substitution at the ring. It is also known that higher temperature and lower bromine concentration increase both the rate of bromination and the relative yield of benzyl bromide. Excess bromine, however, decreases the rate and also favour polar substitution. When weak electron-donating groups,e.g.alkyl, are present, ring bromination is reported to be facile. The presence of electron-withdrawing substituents in benzene tends to stabilise the benzyl radical thereby yielding exclusively the corresponding benzyl bromide.

In an earlier work[14] condensation of toluene to produce *ortho* and *para*-methylphenylmethanes has been effected by the use of bromine/bentonite earth system and the formation of benzyl bromide as a first species is proposed. However, bromination of toluene when catalysed by NaY zeolite in the presence of an epoxide yields almost pure *para*-bromotoluene[15]. Chlorination of aromatics by sulfuryl chloride is catalysed by zeolites[16] and it is possible with appropriate choice of the catalyst, to effect at will, either the ring (or) the side-chain chlorination with very high selectivity.We report herein the results of our studies on bromination of alkylbenzenes (1-7) with bromine in carbon tetrachloride in the presence of K10-montmorillonite. The percentage yield and product distribution are presented in Table 1.

Table 1. Selective Bromination of Alkylbenzenes in the presence of K10-Montmorillonite Clay

		Percentage of			
Substrate	Percentage conversion	side chain brominated product	ring brominated products		
			ortho	*para*	poly
Toluene	100(100)[a]	10(100)	33(0)	67(0)	-
Ethylbenzene	94(98)	25(94+4)[b]	0(0)	69(0)	-
Cumene	84(44)	0(39+5)	0(0)	74(0)	10(0)
ortho-xylene	96(99)	0(97+2)	0(0)	96(0)	-
para-xylene	72(98)	0(83+15)	72(0)	0(0)	-
meta-xylene	73(67)	0(67)	0(0)	73(0)	-
Mesitylene	62(70)	0(0)	62(70)	-	-
Anisole	75(62)	0(0)	0(0)	75(62)	-
Phenol	50(50)	0(0)	0(7)	50(43)	-

[a] Numbers given in parentheses represent the corresponding figures in bromination without clay

[b] Along with the major monobromo derivative, small amount of dibromo derivative is also formed

EXPERIMENTAL

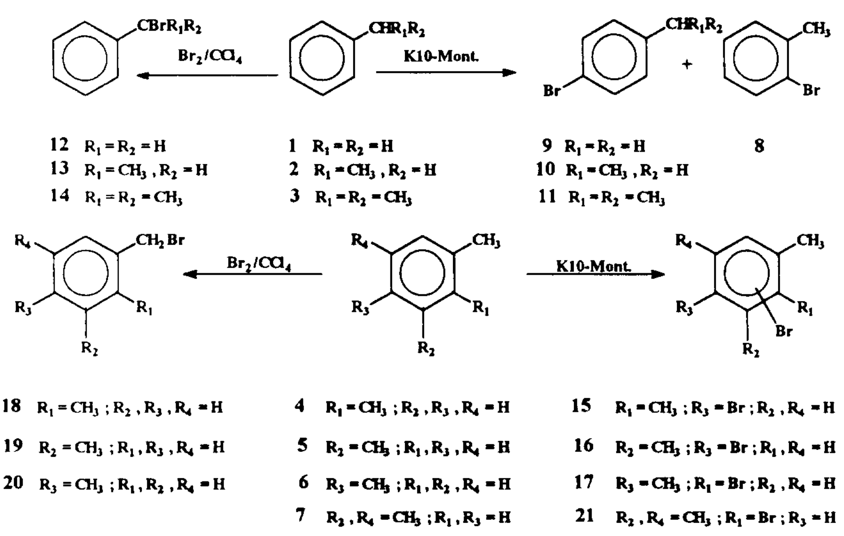
500mg of starting material and 500mg of K10-montmorillonite (Aldrich) clay mixture were taken in a black coated round-bottomed flask fitted with a guard tube and 2ml of dry CCl_4 was added. Equimolar amount of bromine in CCl_4 was added dropwise for thirty minutes, while the mixture was stirred using magnetic stirrer at room temperature. After one hour the reaction mixture was extracted with ether. The residue obtained after evaporation of the ether layer was analysed by HPLC. Identical conditions were employed for bromination of alkylbenzenes in the absence of clay. Brominated products were isolated by a silica gel column using petroleum ether as solvent. ^{1}H NMR (90 MHz) spectra of the different products (δ ppm, TMS) are given below. **8** δ2.4(s,2H),7.1-7.6(complex multiplet, 4H) **9** δ2.2(s,3H), 7.0(AB quartet,2H), 7.3(AB quartet,2H) **10** δ1.4(t,3H),2.3(q,2H),7.1(AB quartet,2H),7.35(AB quartet,2H) **11** δ1.25(d,6H), 2.9(septet,H),7.05(AB quartet,2H),7.4(AB quartet,2H) **12** δ4.4(s,2H),7.3(s,5H) **13** δ2.05 (d,3H),5.22(q, H),7.35(s,5H) **15** δ2.1(s,3H),2.4(s,3H),7.1-7.45(complex multiplet,3H) **16** δ 2.0(s,3H), 7.15(d,H), 7.27(d,H), 7.5(s,H) **17** δ2.0(s,3H), 2.1(s,3H), 6.45(d,H), 7.05(d,H), 6.65(s,H) **18** δ2.40 (s,3H), 4.52(s,2H), 7.20(s,4H), **19** δ 2.35(s,3H), 4.5(s,2H), 7.16(AB quartet,2H),7.30(AB quartet,2H) **21** δ 2.2(s,3H),2.31(s,6H),6.7(s,H) **23** δ3.75(s,3H),6.8(AB quartet,2H),7.4(AB quartet, 2H) **24** δ5.70(s,H),6.85-7.6(a complex multiplet,4H) **25** δ6.1(s, H), 6.75(AB quartet,2H), 7.35(AB quartet,2H).

RESULTS AND DISCUSSION

Bromination of toluene (**1**) using bromine in carbon tetrachloride at room temperature gives benzyl bromide (**12**) as the exclusive product (Scheme I). However, with bromination under similar conditions in the presence of K10-montmorillonite *ortho*-bromotoluene (**8**) (33%) and *para*-bromotoluene (**9**) (67%) are obtained. The remarkable feature of this bromination is absence of benzyl bromide, the side chain brominated product. The formation of *ortho*-bromotoluene is also not reported earlier.

Bromination when extended to ethylbenzene (**2**) and cumene (**3**) provides similar results. Conventional bromination of (**2**) and (**3**) using bromine in CCl_4 yields the α-bromoderivatives (**13** and **14** respectively) along with small amounts of a dibromo compound (as evidenced by GC-MS and is not characterised). Bromination in the presence of K10-montmorillonite results in the formation of ring brominated products and suppression in side chain bromination. Unlike toluene, only *para*-bromo derivatives (**10** and **11** respectively) are obtained as the major products in clay directed bromination and the suppression of *ortho* isomer formation may be explained due to steric crowding in the transition state.

Bromination of *ortho*-xylene(**4**), *meta*-xylene(**5**) and *para*-xylene(**6**) yield only side chain brominated products (**18**,**19** and **20** respectively) in the absence of clay. However, clay-directed bromination of the same result in ring bromination.(**15**,**16** and **17** respectively) Analogues results are obtained with mesitylene, (**7**) wherein clay-directed bromination favour ring brominated product. (**21**)



Scheme I

The results presented above amply demonstrate the efficiency, selectivity and catalytic activity observed in clay directed bromination. While bromination in clay microenvironment results exclusively in aromatic substitution through an ionic mechanism, bromination without clay yields mainly the side chain brominated product involving a radical route.

This selectivity may be attributed to the polar environment in clays which favour electrophilic aromatic substitution and also due to the steric restrictions imposed by the constrained clay microenvironment on the larger transition states in side-chain brominations. Unlike toluene steric effects (small, yet significant because of the restricted environment) play a prominent role in ethylbenzene, cumene, xylenes and mesitylene, by (a) suppressing the side-chain bromination and (b) improving the yield of the *para*-isomer at the expense of the *ortho*-product.

We have carried out the bromination of phenol and anisole also in the presence of clay with a view to improve *ortho*/*para*-selectivity. The results are essentially the same as that of conventional bromination. There is no improvement in yield and also only the *para*-isomer is obtained.

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