



## NOTE

### Regioselective Nitration of Aromatic Hydrocarbons with Bentonite Supported Metallic Nitrates in the Presence of Solid Acids Catalysts

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Toluene and chlorobenzene are mononitrated of good regioselectivities using metallic nitrates as nitrating reagents in the presence of solid acid catalysts. *Para* selectivities are much improved, up to *para*-to-*ortho* ratios of 1.2 for toluene and 5.6 for chlorobenzene respectively.

**Key Words:** Regioselectivity, Nitration, Toluene, Chlorobenzene, Metallic nitrate.

Nitration of aromatic compounds is performed classically with mixtures of nitric and sulfuric acids. In the nitration of substituted benzenes the normal *ortho*- and *para*-substituted derivatives are accompanied by the *meta* isomer and products of polynitration of poor regioselectivity. One of the main goals of modern nitration methodology is to emulate enzymatic efficiency, *i.e.*, a quantitative yield of high regioselectivity under very mild conditions of body temperature and atmospheric pressure. It proved that regioselectivity of aromatic nitration could be improved with solid acids as catalysts. Wright<sup>1</sup> used mixtures of nitric acid and sulfonic resin to improve regioselectivity of nitration of toluene. The reaction result was highly *para* selectivity of ratio of *para*- to *ortho*-nitrotoluene of 1.4 owing to steric effect. Breslow and Campbell<sup>2</sup> used cyclodextrins successfully as the encapsulation of aromatic substrate in an auxiliary inclusion compound in order to block *ortho* attack and favour thus formation of the *para* product. Likewise, Masci<sup>3</sup> obtained significantly improved *para*-selective nitration by complexing nitronium ion with 21-C-7 crown ether. The recent appearance of methods involving the use of reaction catalyzed by K10 montmorillonite clay and various zeolites in nitrating toluene prompts us to report further our results<sup>4-9</sup>.

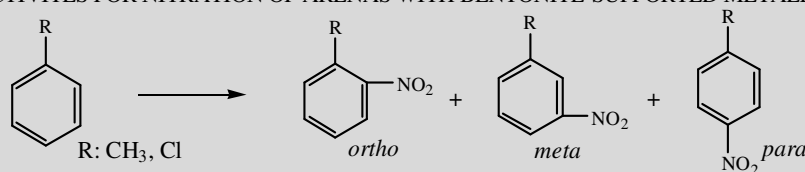
The analyses of arenes and its nitro isomers were carried out by gas-liquid chromatography with a Shimadzu GC-2014C gas chromatography equipped with a hydrogen flame ionization detector and with a 30 m × 0.25 mm i.d. OV-101 glass capillary column with nitrogen as a carrier gas using *n*-dodecane as internal standard. All starting materials were commercially available.

The hydrogen ion-exchanged bentonite catalysts used for supporter were prepared. To 100 mL of a stirred 2 mol/L of sulfuric acid aqueous solution of 10 g of Na-based commercial bentonite were added. Stirring was maintained under reflux temperature for 12 h. The clay suspension was centrifugated and the supernatant solution was discarded and the washing cycles with deionized water were repeated until disappearance of anion ions. The collected acid-modified bentonite, after drying overnight in an oven at 130 °C, was finely ground to pass a 100 mesh screen in a mortar.

Preparation of clay-supported cupric nitrate in the following process, *i.e.*, to a 500 mL pear-shaped evaporating flask was added 15 g cupric nitrate trihydrate and 187 mL acetone. After vigorously stirred for 8 min, 15 g acid-treated bentonite was added and stirring was continued for another 10 min. The evaporating flask was connected to a rotary evaporator and the solvent was eliminated under reduced pressure on a water bath at 48 °C. After 0.5 h, a dry solid crust adhered to the walls of the flask. It was flaked off with a spatula, ground to a powder and the rotary drying under vacuum was resumed for 0.5 h at the same temperature, giving clay-supported cupric nitrate as a light, free-flowing powder. The other clay-supported metallic nitrates were prepared in a similar way to that of clay-supported cupric nitrate.

Followed by nitration of toluene and chlorobenzene. To a round-bottomed flask equipped with a mechanical stirrer added 50 mL toluene, 10 mL acetic anhydride and 10 g clay-supported metallic nitrate. The mixture was stirred vigorously for 12 h at room temperature, after reaction, filtered under reduced pressure. The filter residue was washed with portions

TABLE-1  
REGIOSELECTIVITIES FOR NITRATION OF ARENAS WITH BENTONITE-SUPPORTED METALLIC NITRATES



Nitrates	Nitrotoluene		Nitrochlorobenzene	
	<i>para/ortho</i>	Yield (%) <sup>a</sup>	<i>para/ortho</i>	Yield (%) <sup>a</sup>
Cu(II)	1.2	70	5.6	57
Zn(II)	0.9	76	4.7	60
Cd(II)	1.0	47	4.7	27
Fe(II)	0.9	53	5.1	29
Co(II)	1.1	35	5.1	31
Ni(II)	0.9	37	5.2	29
Al(II)	1.1	28	4.8	26
Bi(III)	0.8	30	4.6	32

<sup>a</sup>The amount of nitroarenes by gas-liquid chromatography using *n*-dodecane as internal standard.

TABLE-2  
RATIO OF *para* TO *ortho* NITRO ISOMERS IN VARIOUS NITRATIONS OF CHLOROGENE

Supported-Cu(NO <sub>3</sub> ) <sub>2</sub>	HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> <sup>14</sup>	AgNO <sub>3</sub> /BF <sub>3</sub> <sup>15</sup>	NO <sub>2</sub> BF <sub>4</sub> /sulfolane <sup>16</sup>
5.6	1.8	1.3	3.5

of solvent. The filtrate was washed with 5 % sodium bicarbonate solution and then with water. The nitro compounds were analyzed by GC with authentic samples after evaporated portions of solvent. For nitration of chlorobenzene was the same as that of toluene besides 16 h of reaction periods. However, 3 mL chlorobenzene substrate was employed under 50 mL solvent media in order to understand solvent characteristics.

In order to activate clay catalysts, result in generation of surface radical sites of the O<sub>3</sub>SiO-silyloxy type and increase their surface acidity<sup>10</sup>, clay supports were calcined for 4 h in an oven at temperature in the range of 100-600 °C before using. Clay-supported cupric nitrate was used to nitration of toluene and chlorobenzene, respectively, under Menke conditions<sup>11</sup>, in order to evaluate catalytic activities and regioselectivities in the nitration reaction. Of the solid catalyst supports selected bentonite compared with kaolinite and celite appear good *para* catalytic selectivity in the nitration of toluene and chlorobenzene, up to ratios of 1.2 and 5.6 respectively in range of 300-500 °C.

For the nature of clay-supported metallic nitrate, on the basis of the determination by Fukunaga' reactivity sequence of 10 metallic nitrates toward aromatic nitration using thermographic methods<sup>12</sup> and Cornelis' reactivity sequence of 13 metallic nitrates toward toluene nitration using K10 montmorillonite catalyst<sup>13</sup>, 8 metallic nitrates were applied to nitrate toluene and chlorobenzene using modified bentonite with sulfuric acid as support of reaction time of 13 h for toluene and 35 h for chlorobenzene respectively. From Table-1 modified bentonite-supported cupric nitrate is of better reactivity and regioselectivity which can also be compared with some general processes shown in Table-2.

Various solvents involving *n*-hexane, cyclohexane, carbon tetrachloride, chloroform, methylene dichloride, 1,2-

dichloroethane and acetonitrile were run the reaction for toluene selective-nitration under comparable conditions. Out of a range of solvents tried toluene and carbon tetrachloride appeared to be the optimum solvents, giving rise to the highest yields and best selectivities as also observed by Cornelis *et al.*<sup>13</sup> and Smith *et al.*<sup>17</sup> in related reactions.

## Conclusion

To sum up, a highly *para* regioselective nitration for arenes can be achieved by employing acidic bentonite-supported metallic nitrates as nitrating agents and a mild reaction conditions can be easily conducted in industrial preparation process.

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