Friedel-Crafts Benzylation using Clay Mineral Catalysts and New Synthesis of Metal Complex Dyes

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Summary: Friedel-Crafts benzylation of toluene, naphthalene, anthracene, nitrobenzene, quinoline, 8-hydroxy quinoline and pyridine have been carried out in presence of clay mineral catalyst obtained from Pakistani clay minerals. Benzyl group peaks [m/e 91 and m/e 89] were found present in the mass spectra taken of all the benzylated compounds. Quinoline and 8-hydroxy quinoline extracted iron and aluminum from the clay mineral catalyst and made metal complex dyes. Benzoylation of 8-hydroxy quinoline also yielded metal complex dye. This is a unique reaction and has not been reported previously. It was found that quinoline and 8-hydroxy quinoline formed metal complex dyes are suitable for dying polyester or synthetic fiber. Benzyl toluene, benzyl anthracene and benzyl naphthalene were formed in good quantity. Benzyl anthracene dimerized during reaction and benzyl nitrobenzene polymerized. Benzyl pyridine yields impure compound.

Introduction

The catalytic effects of clay minerals for the synthesis of organic compounds were long ago recognized as having fundamental importance in petroleum cracking reactions and in chemical synthesis of certain organic compounds. In past 40 years immense literature has developed on the properties of various clay minerals or solid acids for the synthesis of various organic compounds [1]. The catalytic activity and selectivity have been extensively studied in the last decade. The solid acids catalysis is one of the most promising economical and ecological fields. They non corrosive and environmentally benign, present fewer problems for their disposal, their repeated use is possible and their separation from liquid is much easier. Therefore the replacement of the homogenous catalysts with the heterogeneous ones is becoming even more so important in chemical and life science industry. At present more than 100 solid acids, based on oxides and complex oxides have been developed for use in industry [1]. Only four catalysts based on the clay minerals are in use. Clay minerals are also complex oxides as well as carbonates and silicates [1].

Pakistan is rich in mineral wealth. The catalytic activity of number of clay minerals was evaluated [2]. It was observed that some of the clay mineral showed good catalytic activity with and without acid activation. But some other clay minerals did not show any catalytic activity even after acid activation. The chemical composition of clay minerals shows that the presence of transition metals was responsible for the catalytic activity of clay minerals.

The acid treatment of clay mineral replaces the exchangeable cations (K^+, Na^+, and Ca^+) by H^+ ions in the interlamellar space and also leaches out a part of Al^{3+}, Fe^{3+}, and Mg^{2+} ions from octahedral sheet of lattice structure, which renders clay physically more porous and electrochemically more active [3].

It is observed that the absence of transition metals such as iron and titanium in the clay minerals results in reduced catalytic activity or no activity. Acid activation did not increase the catalytic activity of such type of clay minerals rather it totally made them inactive. This led us to the spectroscopic analysis of clay minerals which shows the presence of transition trace metals also [4].

These clay minerals have moderate catalytic activity as compared to aluminum chloride. Hence polymerization and poly-substitution is not possible. This property led us to synthesize compounds like 9, 10 dihydro-anthracene, biphenyl methane, o- and p-hydroxy biphenyl methane, 1-benzyl 2-naphthol and 4-benzyl 1-naphthol [3, 5]. The chemical and spectroscopic analysis of the catalyst is reported in this paper (Table-1).

Table-1: Chemical composition and trace metal analysis of catalyst

Sr No	Trace Elements	mg / kg	Elements	% age composition
1	As	32	SiO_2	11.84
2	Cd	9	Al_2O_3	29.53
3	Co	93	Fe_2O_3	37.50
4	Cr	941	TiO_2	4.75
5	Cu	137	Na_2O	0.90
6	Mn	308	MgO	1.51
7	Ni	50	CaO	3.50
8	Pb	61	Loss on ignition	10.12
9	Se	0.8		
10	Zn	165		

All those compounds which make complexes either polymerize, poly-subtitute or are destroyed with aluminum chloride and they cannot be benzylated or alkylated by using aluminum chloride. Examples are pyridine, quinoline, 8-hydoxy quinoline, naphthalene, anthracene [6]. A detailed study is reported for the benzylation of these organic compounds using clay minerals as catalysts.

Results and Discussion

The clay mineral catalysts are solid acid catalyst and benzyl chloride is a liquid. The physical form of the third component of chemical reaction has profound influence on the course and rate of the reaction. When the reactants are solids such as naphthalene, anthracene, and 8-hydroxy quinoline the reaction proceed slowly simply because the reacting species have difficulty in getting together. When one of the reactant is liquid such as quinoline, pyridine, toluene and nitrobenzene the reaction rate is improved, since the opportunity for the intimate mixing of reactants is increased, especially if the solid reactant is miscible with benzyl chloride the rate of reaction is further improved.

Mass spectra of the products synthesized were recorded. The molecular ions peaks of the benzyl group is significant and showed peaks at *m/e* 89 and 91. [7] and were present in all the spectra of the compounds synthesized in this study. This confirmed that the benzylation of the organic compounds has taken place with the clay mineral catalyst.

Benzylation of quinoline and 8-hydroxy quinoline yielded intense colored compounds having low solubility in water. These colored compounds are soluble in alcohol and acetone. When evaluated by dye experts it was found that they are suitable for dying of polyester fabric. It may be pointed out that the color reaction of substituted quinolines and 8-hydroxy quinolines with the metal always resulted in the form of precipitates. Substituted quinoline and 8-hydroxy quinoline are used to form color complexes for determination of metals. Simple quinoline was not used for color reaction [8]. In this study we observed that benzylation of quinoline has taken place and then metal complex are formed giving intense red color. These compounds can be classified as metal complex (disperse) dyes. They have commercially acceptable shade and color. The presence of metals in those compounds was analyzed by ICP. The benzylated quinoline formed red colored iron pigment. While benzylated 8-hydroxy quinoline formed dark green pigment with aluminum. The benzoylated 8-hydroxy quinoline formed blue green pigment with aluminum (Table-2).

Table-2

Reaction	Dye color	λ_{max}	Metal extracted	% age of metal extracted
Benzyl chloride + quinoline	Red dye	439 cm^{-1}	Iron	16.11 %
Benzyl chloride + 8-hydroxy quinoline	Dark green dye	625 cm^{-1}	Aluminum	8.38 %
Benzoyl chloride + 8-hydroxy quinoline	Green dye	386 cm^{-1}	Aluminum	5.90 %

The metal has been extracted from the non ionic catalyst. This selective property of quinoline and 8-hydroxy quinoline has not been reported previously. All the color reactions reported with 8-hydroxy quinoline are with ionic salts. 8-Hydroxy quinoline and substituted quinoline had been used for the estimation of aluminum, chromium, copper, zinc and gallium in analytical chemistry. Unsubstituted quinoline color reactions are not reported in literature. 8-Hydroxy quinoline forms green black precipitate with iron [8].

Mass spectra of the benzylated quinoline pigment shows peaks at *m/e* 91, 126, 163, 176, 296 and 355. The molecular weight peak is at 355.

The mass spectra of benzylated 8-hydroxy quinoline pigment shows *m/e* 89, 117, 145, 181, 207, 234, 253 and 341 respectively. The Molecular weight peak is at 341. The benzoylation of 8-hydroxy quinoline yielded a green color dye. Mass spectra of

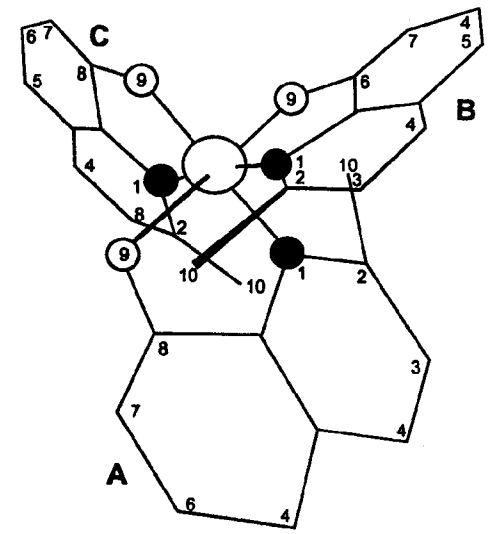

Fig. I

benzoylated 8-hydroxy quinoline showed peaks at *m/e* 91 (benzyl ion peak), 133, 163, 267, 303 and molecular ion peak at 358.

It is well known that aluminum forms a stable complex of stoichometric compositions with 8-hydroxy quinoline, which permits of its determination by gravimetric, volumetric, and absorptionmetric procedure. Tris-(8-hydroxy quinoline) aluminum complex has been assigned the structure given in the figure 1 [8]. But our GC-MS study does not support this structure. Tris-(8-hydroxy quinoline) aluminum complex is used in the manufacturing of organic light emitting diodes. Indium-tin-oxide and tris-(8-hydroxy quinoline) aluminum complex layer act as an anode while LiF/Al or Mg: Ag/Ag and LiF/Mg act as cathodes in the manufacturing of OLED [9].

Benzylation of toluene has been investigated by a number of workers using various clay catalysts to evaluate the catalytic property of their clay mineral catalyst [10]. We have studied the benzylation of toluene and our results are as follows. Yield of benzylated toluene is about 80%. Its GC-MS shows *m/e* 91, 115, 166 and molecular ion peak at 181. Benzyl toluene is used as a starting material for the production of anthraquinone. No poly-substitution takes place.

Benzylation of naphthalene was also studied by us. The yield of benzylated naphthalene is 59.17 %. Benzyl naphthalene mass spectra shows peaks at *m/e* 91(benzyl ion), 115, 141, 165, 203 and molecular weight peak at 218. When compared with mass spectra of benzyl naphthalene mass spectra present in NIST 98 Mass spectra library showed it to be a similar spectra. The mass spectra showed that no poly-substitution has taken place. Benzyl naphthalene compounds have estrogen inhibitory property [11].

The mass spectrum of benzyl anthracene shows a very high intensity molecular ion peak at *m/e* 268. It is also the base peak. Benzyl ion shows peak at *m/e* 91 and benzene at *m/e* 74 [7]. The anthracene has the ability to dimerise in presence of light [12]. Even the substituted anthracene dimerises. The yield of benzyl anthracene is 55.94 %. The elecrophilic substitution mostly occurs at 9 & 10 positions. The dimer reverts to anthracene when heat is applied to it. The compound is insoluble in alcohol but soluble in benzene and toluene. It has high melting point above 350 °C. No poly-substitution has taken place

Molecular ion peak of aromatic nitro compounds is strong and permanent peak resulted from elimination of NO_2 group (M-46). Benzyl ion peak is at 91 and of a neutral molecule with a rearrangement to form a phenoxy cation. M-30 is a diagnostic peak of NO^+. This compound is formed with a lot of heat generated during polymerization and explosion occur. It is insoluble in alcohol and soluble in benzene, toluene and chloroform. It is not possible for the nitrobenzene to polymerize to amines as discussed in paper by paul sigal *et al.*, [13]. Benzyl pyridine mass spectra showed peaks at *m/e* 91(benzyl ion), 125, 163, 215, 238, 253, 279, 310, 349, 378 and molecular ion peak at 395. This compound appears to be impure.

Experimental

The compounds were synthesized using clay catalyst (Table-1) GC-MS spectra of these compounds were recorded on Varian's GC-MS spectrometer. IR of the compounds was taken using Hitachi IR spectrophotometer model No:27030 and λ_{max} of the dyes were taken using Shimadzhu UV-Vis spectrophotometer.

Metals in the compounds were analyzed using Varian Vista-MPX CCD simultaneous ICP-OES model 1998.

The compounds whose structure is known their % age yield is given. However the compounds

whose structure is not known only there weight is given.

Red metal complex dye

Quinoline (11.8 ml, 0.1 mole) and benzyl chloride (11.50 ml, 0.1 mole) were taken in a round bottom flask. catalyst (5-10 gm) was added and then mixture was refluxed on hot plate with constant stirring at a temperature range of 120 °C- 130 °C. The reaction was completed in about 1-hour. After the completion of the reaction the compound was dissolved in alcohol, filtered and distilled to obtain a red color metal complex dye (λ_{max} = 439 cm^{-1}). The amount of dye obtained from the reaction is 12.6 gm. IR (KBr, cm^{-1}) 3376 (N-H stretching vibration, 3040 C-H stretching vibration, 1528 (C=N stretching vibration) GC-MS Spectra of the compound showed peaks at *m/e* 91 (benzyl ion), 126(quinoline ion), 163, 176, 296 and molecular ion peak at 355. The amount of iron in the dye was determined with the help of ICP.

Dark green metal complex dye

8-hydroxy quinoline (14.51gm, 0.1 mole) and benzyl chloride (11.5 ml, 0.1 mole) were taken in a round bottom flask. Clay Catalyst (10 gm) was added and then mixture was refluxed on a hot plate with constant stirring at a temperature range of 150 °C-160 °C. The reaction was completed in about 1- hour. After the completion of the reaction the compound was dissolved in alcohol and filtered. After the removal of alcohol by distillation a dark green color metal complex dye (λ_{max} = 625 cm^{-1}).was obtained. The amount of dye obtained from the reaction is 13 gm. IR (KBr, cm^{-1}) 3376 (O-H stretching vibration), 2876 (C-H stretching vibrations), 1580 (C=N stretching vibration). 1492 (C-H deformation vibrations) 1302 (C-H deformation vibrations of substituted pyridines). GC-MS Spectra of the compound showed peaks at *m/e* 89 (benzyl ion), 117, 145, 282 and molecular ion peak at 341. The amount of aluminum in the dye was determined with the help of ICP.

Green metal complex dye

8-Hydroxy quinoline (14.51 gm, 0.1 mole) and benzoyl chloride (11.6 ml, 0.1 mole) were taken in a round bottom flask. Clay Catalyst (5-10 gm) was added and then mixture was refluxed on a hot plate with constant stirring at a temperature range of 150 °C-160 °C. The reaction was completed in about 1-hour. After the completion of the reaction the compound was dissolved in alcohol and filtered. After the removal of alcohol by distillation a green color metal complex dye (λ_{max} = 386 cm^{-1}) was obtained. The amount of dye obtained from the reaction was 8 gm. IR (KBr, cm^{-1}) 3308 (O-H stretching vibration), 2876 (C-H stretching vibrations), 1846 (C=O stretching vibrations), 1682 (C=C stretching vibrations) 1580 (C=N stretching vibration). 1456 (C-H deformation vibrations) 1302 (C-H deformation vibrations of substituted pyridines). GC-MS Spectra of the compound showed peaks at *m/e* 91 (low intensity), 133, 164,203, 267 and molecular ion peak at 358. The amount of aluminum in the dye was determined with the help of ICP.

Benzyl toluene

Toluene (30 ml) and benzyl chloride (11.50 ml, 0.1 mole) were taken in a round bottom flask. Catalyst (5-10 gm) was added and then mixture was refluxed on hot plate at a temperature range of 150-170 °C. The reaction was completed in 1 hour. After the completion of the reaction the compound was dissolved in excess of toluene and filtered to remove catalyst. Toluene was distilled off to obtain a liquid compound. Yield 80 %, b.p 280 °C. IR (KBr, cm) 3008 (C-H stretching vibration), 2908 (aromatic C-H stretching vibrations), 1888 (C=C stretching vibrations), 1072 (CH_3 rocking vibrations). The GC-MS spectra showed peaks at *m/e* 91 (benzyl ion), 115, 166 and molecular ion peak at 181. The mass spectrum of the benzyl toluene was compared with the mass spectrum of Benzyl Toluene present in NIST 98 MS Library Database. Both the spectra are identical.

Benzyl naphthalene

Naphthalene (12.90 gm, 0.1 mole) and benzyl chloride (11.50 ml, 0.1 mole) were taken in a round bottom flask. Catalyst (5-10 gm) was added and then mixture was refluxed on hot plate at a temperature range of 160-170 °C. The reaction was completed in 1 hour. After the completion of the reaction the compound was dissolved in chloroform and filtered to remove catalyst. Yield 59.17 %, BP > 322 °C.

IR [KBr, cm^{-1}] 3022 (C-H stretching vibration), 2908 (aromatic C-H vibration), 1590

(C=C stretching vibration), 1434 (C=C ring stretching vibration), 1260 (CH_2 wagging vibration), 696 (Anthracene ring vibrations).

GC-MS spectra of the compound showed peaks at *m/e* 91(benzyl ion), 115, 141, 165, 203 and molecular weight peak at 218. The mass spectrum of the Benzyl Naphthalene was compared with the mass spectrum of benzyl naphthalene present in NIST 98 MS Library Database. Both the spectra are identical.

Benzyl anthracene

Anthracene (17.82 gm, 0.1 mole) and benzyl chloride (11.50 ml, 0.1 mole) were taken in a round bottom flask. Clay catalyst (10 gm) was added and then the mixture was refluxed on a hot plate with constant stirring at a temperature range of 150 °C-160 °C. The reaction was completed in 1 hour. After the completion of the reaction compound was washed with alcohol and dissolved in chloroform and filtered to remove catalyst. Chloroform was distilled on water bath to obtain a pure compound. Yield = 55.94 %. IR (KBr, cm^{-1}) 2144 (C=C stretching vibrations), 1926 (C=C symmetric vibration), 1622 (Anthracene ring vibration). The GC-MS spectra of the compound showed peaks at *m/e* 74, 91(benzyl ion), and molecular ion peak at 268. The mass spectrum of the Benzyl Anthracene was compared with the mass spectrum of benzyl anthracene present in NIST 98 MS Library Database. Both the spectra are identical.

Benzyl Nitrobenzene

Nitrobenzene (10.2 ml, 0.1 mole) and benzyl chloride (11.50 ml, 0.1 moles) were taken in a round bottom flask. Catalyst (5-10 gm) was added and then mixture was refluxed on hot plate at a temperature range of 100-120°C. The reaction was completed in 1 hour. After the completion of the reaction the compound was separated from catalyst with the help of ethyl alcohol. The amount of compound obtained was 8.0 gms. The compound obtained after the removal of alcohol showed IR [KBr, cm^{-1}] 3544, 3388, 3252, 2696, 2432, 1910, 1562, 1150. The GC-MS spectra of the nitrobenzene showed peaks at *m/e* 77, 91 (benzyl ion), 105, 155, 183 and molecular ion peak at 243. It appears the compound obtained is *a* polymer.

Benzyl pyridine

Pyridine (8.0 ml, 0.1 mole) and benzyl chloride (11.50 ml, 0.1 mole) were taken in a round bottom flask. Catalyst (5-10 gm) was added and then mixture was refluxed on hot plate at a temperature range of 160-170 °C. The reaction was completed in 1 hour. After the completion of the reaction the compound was separated from catalyst with the help of ethyl alcohol. The compound left after the removal of alcohol had b.p 203-205 °C % age yield = 59.24 %. IR [3316 cm (N+ - H stretching vibrations), 2026 cm (C=N stretching vibrations), 1614 cm (C=C stretching vibrations). The GC-MS spectra of the compound showed peaks at *m/e* 91 (benzyl ion), 125, 163, 215, 238, 253, 279, 310, 349, 378 and molecular ion peak at 395. It appears that compound is impure.

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