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Green and efficient diazotization and diazo coupling reactions on clays

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Abstract

Diazotization and diazo coupling reactions of sodium sulfanilate dihydrate and *para*-diazonium benzene sulfonyl azide with aromatic phenols over eco-friendly clay catalysts are described. These inexpensive, noncorrosive and reusable catalysts were found to exhibit bifunctional catalytic properties for diazotization and diazo coupling reactions. No considerable decreases in the efficiency of the catalysts were observed after four cycles of operation. The new method totally avoids the use of acids, alkalies and toxic solvents in diazotization and diazo coupling reactions.

Keywords: Azo dyes; Diazotization; Diazo coupling; Clays; Green chemistry

1. Introduction

Azo dyes are compounds that contain azo groups linked to methine or aromatic sp^2-hybridized C-atoms. The formation of diazotizing reagent starts with protonation of nitrous acid under strongly acidic conditions, and azo coupling carried out at low temperature in the presence of nucleophilic coupling components, the reactivity of a nucleophilic substrate increases with increasing basicity phenolates and amines [1]. These conventional acid–base catalyzed processes are effective for the near quantitative formation of the desired products. But the main limitation of such synthetic processes is their environmental incompatibility. The acidic and basic effluents from the laboratory and industry produce permanent damage to the environment and disturb the ecological balance [2]. In recent years, clay based catalysts are reported to be effective for performing many of the acid–base catalyzed organic reactions in a better, environmentally benign manner [3,4]. Recently, we reported new azoic dyes containing (1H)-tetrazol and imidoyl azide group [5]. As part of our ongoing research program for exploring the bifunctional catalytic properties, we herein describe a new process for diazotization and diazo coupling reactions using clay based layered silicates as a catalyst toward the synthesis of azo dyes.

2. Results and discussion

This pape\r describes the facile and modified synthesis of azo dyes (this method previously has been reported under acidic and basic conditions) [6] without using conventional acid or base in the presence of clays. In the present synthesis, the sodium sulfanilate or 4-aminobenzene sulfonyl azide was first made into a paste with clay catalyst and it was then cooled to 0–5 °C, as shown in Scheme 1.

This clay mixture was then diazotized with dilute $NaNO_2$ solution. The diazonium–clay complex formed was subsequently coupled with phenols, naphthols and an aromatic amine. The sodium sulfanilate azo dye formed was separated from the catalyst by extracting it into water or alcohol and sulfonyl azide azo dye was separated from the catalyst by extracting it into acetone and from where it was recovered by removal of the solvent under vacuum. The generality of the process is proved by performing the reaction with all the three catalysts, with sodium sulfanilate or 4-aminobenzene

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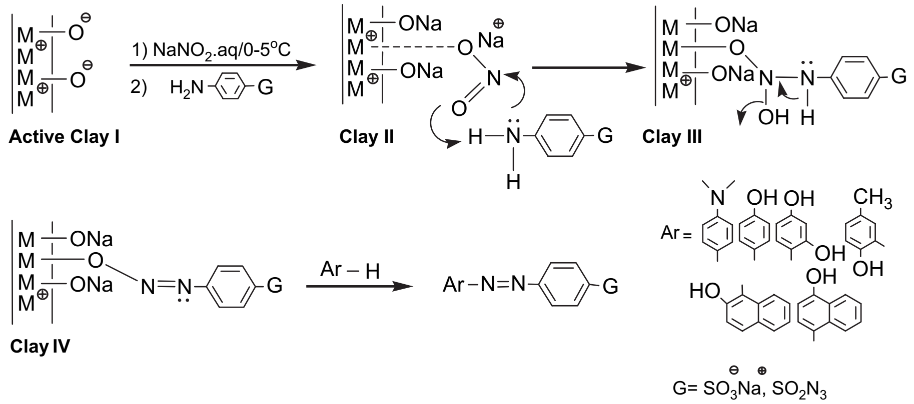
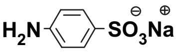
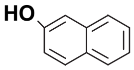
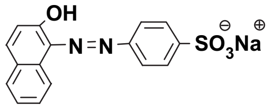
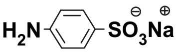
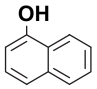
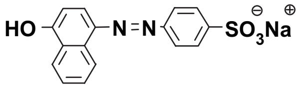
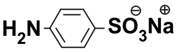
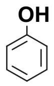
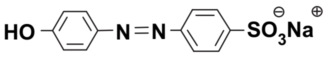
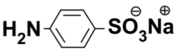
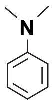
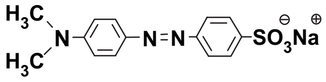
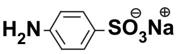
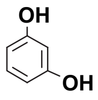
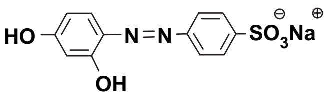
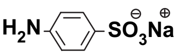
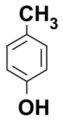
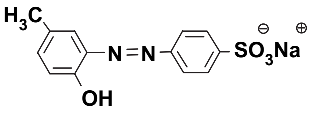


Scheme 1.

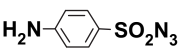
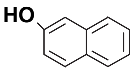
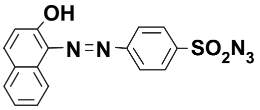
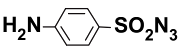
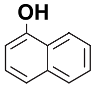
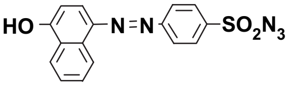
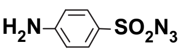
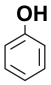
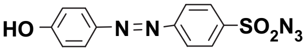
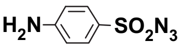
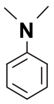
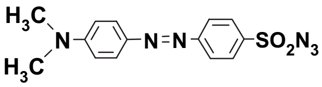
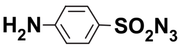
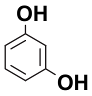
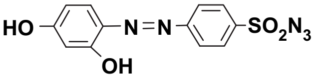
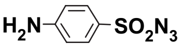
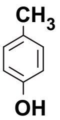
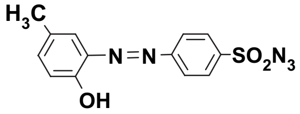
sulfonyl azide and with coupling agents. After the formation of the diazonium–clay complex, the edge hydroxyls of the clay platelets are believed to get converted into –ONa species by consuming the Na ions from $NaNO_2$ solution used for diazotization. This –ONa species helps to maintain the pH of the medium neutral or slightly alkaline for a quantitative coupling of the diazonium ion with the coupling agent. In almost all the cases, the isolated yields of the pure products were found to be near quantitative as outlined in Tables 1 and 2. Control reactions were carried out with the same reagents in the presence of mineral acids like HCl and bases by following the conventional procedure for comparing the yields. All substrate yields for sodium sulfanilate dyes are in the range of 60–85% and for sulfonyl azide dyes in the range of 30–60%. The yields found to be slightly less than the same obtained from the present mineral acids process. Recycling of the catalysts was also investigated. For this purpose, the catalysts after the removal of the azo dyes were washed several times with acetone and dried at 110 °C in an air oven for 1 h. These oven-dried samples were then calcined at 450 °C for 3 h in a furnace and used for performing the reactions. This process was repeated 4 times and no considerable decreases in the yield of the azo dyes were observed. The results obtained for the recycling reactions are given in Tables 3 and 4. The mechanism for diazotization and diazo coupling reactions is depicted in Schemes 1 and 2. This mechanism was proposed

Table 1
Diazotization and diazo coupling reactions of sodium sulfanilate dehydrate with some aromatic phenols over bentonite, kaolin and K10

Azo dyes	Amine	Coupling agent	Product	%Yield		
				K10	Bentonite	Kaolin
1[a]				85	75	80
2[a]				80	70	75
3[b]				80	74	78
4[c]				85	77	79
5[b]				65	60	62
6[d]				70	60	65

The structure of all dyes were reported previously in Refs. (a) [6a], (b) [6b], (c) [6c], and (d) [6d].

Table 2
Diazotization and diazo coupling reactions of *para*-amino benzene sulfonyl azide with some coupling components over bentonite, kaolin and K10

Azo dyes	Amine	Coupling agent	Product	% Yield		
				K10	Bentonite	Kaolin
7				60	50	55
8				55	45	50
9				50	40	45
10				45	35	40
11				38	30	35
12				50	40	45

The structure of all dyes was reported previously in Refs. [6e–h].
[a]Isolated yields.

based on our new transition state model for the elimination reactions of alcohols over aluminum oxides and thorium oxide [7]. Initially, clay is activated by losing water molecules to retain acidic and basic sites I, next $NaNO_2$ adsorbs over the surface of the clay on acidic sites II. In the next stage, amino group of sodium sulfanilate initiate a nucleophilic addition reaction with the adsorbed NO_2 to produce intermediate II. Elimination of water (by clay) from III gives IV. Rearrangement of IV on the surface of clay produces the adsorbed diazonium salt V. Finally, the added coupling agent adsorbs by the surface of the clay (which is carrying the adsorbed diazonium salt V) forming new intermediate VI. Deprotonation from the adsorbed azo intermediate VI is followed by desorption of azo dye from the inactive catalyst VII.

Absorption spectra of azo dyes were recorded in various solvents and the results are summarized in Tables 5 and 6. The color of these azo dyes depends on the nature of both the diazo and coupling components. The naphthyl sulfonyl azides have characteristic absorption peaks at 223, 313 and 479 nm. The peaks at 223 and 313 nm originate from the aromatic rings, and the peak at 479 nm reflects the conjugated

Table 3
Results of the recycling reactions

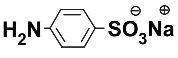
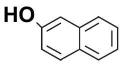
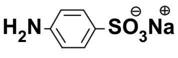
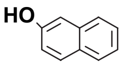
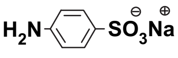
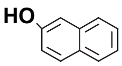
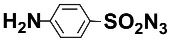
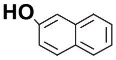
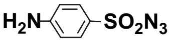
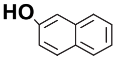
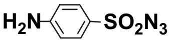
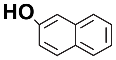
Catalyst	Amine	Coupling agent	% Yield			
			I cycle	II cycle	III cycle	IV cycle
K10			95	95	90	85
Bentonite			85	85	75	70
Kaolin			90	88	80	71

Table 4
Results of the recycling reactions

Catalyst	Amine	Coupling agent	% Yield[a]			
			I cycle	II cycle	III cycle	IV cycle
K10			90	90	85	80
Bentonite			80	80	75	70
Kaolin			85	80	75	70

[a]Isolated yields.

structure formed by azo bond. The absorption maxima of the azo dyes under investigation showed larger bathochromic shifts in DMF than in other solvents.

The IR spectra of the prepared azo dyes showed the characteristic absorption peaks due to stretching frequency of the OH group in the region of 3427–3545 cm^{-1} and the stretching frequency of the N_3 group in the region of 2110–2150 cm^{-1}, for the azo dyes **7**, **8**, **9**, **10**, **11** and **12**. Absorption peak in the region of 1370–1519 cm^{-1}, attributed to $\nu_{N=N}$, while the observed peak in the region of 1221–1397 cm^{-1} was due to the ν_{SO_2}, as outlined in Table 7. The ^1H and ^{13}C NMR data for the azo dyes are given in Table 8.

3. Conclusions

To summarize, we have developed a highly efficient 'green' method for synthesis of azoic dyes catalyzed by eco-friendly clay catalysts (bentonite, kaolin and K10) with better recycling options with high yields. This method totally avoids the use of acids, alkalies or toxic solvents in diazotization and diazo coupling reactions.

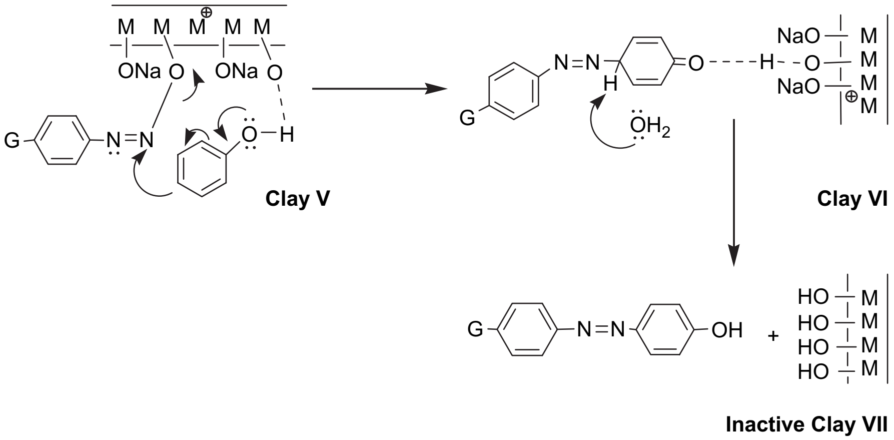
4. Experimental

4.1. Materials and instrumentation

Bentonite and montmorillonite K10 are procured from Aldrich and kaolin from Acros. The sodium sulfanilate was obtained from Merck and used as such. Melting points reported were determined by open capillary method. UV spectra were recorded on a JASCO V-570 UV/Vis/NIR spectrophotometer. IR spectra were recorded on a JASCO FT/IR-680 PLUS spectrometer. NMR spectra were recorded on a Bruker 500 ultrasheild NMR (DMSO-d_6 used as solvent).

4.2. Preparation of bentonite and kaolin clay catalysts

All catalysts were activated with 2 M HCl in the solid to liquid ratio 1:4 (400 ml, 2 M HCl for 100 g clay) for a period of 45 min and filtered. It was then washed thoroughly with distilled water for removing chloride ions and dried in an air oven at 110 °C for 2 h. Then acid activated clay was again calcined at 430 °C for a period of 2 h and used for the reaction.



Scheme 2.

Table 5
UV–visible spectra of sodium sulfanilate azo dyes

Azo dyes	H_2O/λ_{max}	Ethanol/λ_{max}	DMF/λ_{max}
1	248, 312,483	246, 310, 481	483
2	247, 346, 479	369, 471	379, 477
3	248, 354	356	359
4	271, 464	416	423
5	278, 423	356	365
6	326	328	336

4.3. Preparation of azo dyes

4.3.1. Representative procedure for diazotization and diazo coupling reaction for sodium sulfanilates *1–6*

A typical experiment, 4.2 g of (2 mmol) of sodium sulfanilate was adsorbed on 5 g of clay catalyst and cooled to 0–5 °C. To this mixture, 2.76 g (4 mmol) of $NaNO_2$ in (15 ml) H_2O was added dropwise for a period of 1 h and then 5 mmol of phenols was added to this ice-cold diazonium–clay complex. This solution was brought to room temperature with constant stirring and kept at room temperature for 1 h. The reaction mixture was then repeatedly extracted into water. Water extracts were evaporated under vacuum. ^1H NMR, ^{13}C NMR, IR, m.p., mass analysis, isolated yields and appearance for dyes **1–12** are listed in Tables 7 and 8.

4.3.2. 4-Acetamidobenzenesulfonyl azide

4-Acetamidobenzenesulfonyl chloride (48.6, 208 mmol) was dissolved in 500 ml acetone and the solution was cooled to a temperature of 0 °C over a period of 60 min, a chilled aqueous solution of sodium azide (20 g, 312 mmol, 200 ml) was added dropwise and the resultant solution allowed to stir for a further 60 min at that temperature. The solution was then poured onto an ice/water slurry (1.5 L) and the white precipitate was collected at the pump, washed with ice-cold water and dried under vacuum, 4-Acetamidobenzenesulfonyl azide could be used in the next step directly, recrystallized from a solution of acetone and water giving 4-acetamidobenzenesulfonyl azide as white crystals. Yield: 75%; m.p. 108–110 °C; FTIR (KBr) 2125, 1674, 1160 cm^{-1}; ^1H NMR (DMSO-d_6): δ 8.4 (1H, s, NH), 7.82 (4H, d, $J = 8.3$ Hz, phenyl), 2.23 (3H, s, CH3); ^{13}C NMR (DMSO-d_6): δ 69.5, 144.1, 132.3, 128.9, 119.6, 24.7; *m/z* 240 [M^+].

Table 6
UV–visible spectra of sodium sulfanilate azo dyes

Azo dyes	Ethanol/ λ_{max}	Acetone/ λ_{max}	DMF/ λ_{max}	DCM/ λ_{max}	Acetonitrile/ λ_{max}
7	223, 310, 478	223, 310, 478	223, 311, 479	224, 313, 479	223, 309, 474
8	366, 493	362, 493	363, 498	221, 368, 496	364,491
9	371	365	373	356	361
10	455	459	471	463	460
11	420	415	427	420	416
12	415	412	425	420	425

4.3.3. 4-Aminobenzenesulfonyl azide

4-Acetamidobenzenesulfonyl azide (12 g, 5.1 mmol) and 45 ml concentrated HCl were heated at reflux for 35 min, upon cooling to approximately 0–5 °C. The solution was neutralized with saturated sodium bicarbonate solution and solid sodium bicarbonate until a pH of approximately 6 was reached. The light brown mixture was extracted with diethyl ether, washed, dried ($MgSO_4$) and then filtered. Evaporation of the diethyl ether solution provided a brown solid which could be recrystallized from a small portion of diethyl ether. Yield: 70%; FTIR (KBr) 3480, 2126, 1160 cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.2 (4H, d, $J = 8.4$ Hz, phenyl), 4.37 (2H, s, br, $-NH_2$); ^{13}C NMR (DMSO-d_6): δ 152.5, 129.9, 125.3, 114; *m/z* 198 [M^+].

4.3.4. Representative procedure for diazotization and diazo coupling reaction for para-diazonium benzene sulfonyl azides *7–12*

In a typical experiment, 1.98 g (1 mmol) of 4-aminobenzene sulfonyl azide was adsorbed onto 3 g of clay catalyst and cooled to 0–5 °C. To this, 1.38 g (2 mmol) of $NaNO_2$ in 15 ml H_2O was added dropwise for a period of 1 h. After the addition of $NaNO_2$, 1 mmol of nucleophilic coupling components were added to this ice-cold diazonium–clay complex after the addition mixture was stirred for 3–4 h and then filtered. The sulfonyl azide dye formed was separated from

Table 7
Characterization of azo dyes

Azo dyes	Molecular formula	m.p. (°C)	Appearance	Mass *m/z*	IR ν_{max} (cm^{-1}, KBr)
1	$C_{16}H_{11}N_2NaO_4S$	162–164	Orange	350 (M^+)	3451, 1621, 1565, 1391, 1171
2	$C_{16}H_{11}N_2NaO_4S$	>300	Orange-red	350 (M^+)	3427, 1634, 1537, 1364, 1179
3	$C_{12}H_9N_2NaO_4S$	>300	Yellow	327 (M^+)	3513, 1621, 1505, 1397, 1176
4	$C_{14}H_{14}N_3NaO_3S$	>300	Red-brown	300 (M^+)	3436, 1608, 1519, 1367, 1121
5	$C_{12}H_9N_2NaO_4S$	>300	Yellow-brown	316 (M^+)	3463, 1627, 1509, 1339, 1123
6	$C_{13}H_{11}N_2NaO_4S$	>300	Orange-brown	314 (M^+)	3441, 1618, 1535, 1361, 1132
7	$C_{16}H_{11}N_5O_3S$	172–174	Red	353 (M^+)	3545, 2110, 1379
8	$C_{16}H_{11}N_5O_3S$	182–184	Red	353 (M^+)	3433, 2144, 1371
9	$C_{12}H_9N_5O_3S$	134–136	Yellow	303 (M^+)	3455, 2137, 1361
10	$C_{14}H_{14}N_6O_2S$	160–162	Orange-red	330 (M^+)	2110, 1350
11	$C_{12}H_9N_5O_4S$	172–174	Yellow-brown	319 (M^+)	3468, 2125, 1370
12	$C_{13}H_{11}N_5O_3S$	118–120	Orange	317 (M^+)	3450, 2120, 1370

Table 8
NMR data δ (ppm) of azo dyes in (DMSO-d_6)

Azo dyes	^{1}H NMR	^{13}C NMR
1	8.14 (1H, s, −OH); 7.35 (4H, d, $J = 9.3$ Hz, phenyl sulfonate); 7.15−8.99 (6H, m, naphthyl)	21, 123(2), 124, 125, 127(2), 127.7, 128, 128.3, 129, 133, 139, 146, 155, 171.
2	7.85 (1H, m, −OH); 8.18 (4H, d, $J = 8.2$ Hz, phenyl sulfonate); 7.31−8.59 (6H, m, naphthyl)	110, 122, 123.5, 123.5, 123.8, 124, 124.9, 125, 127.6, 127.6, 129, 145, 145.4, 155.8, 157, 159.9.
3	10.4 (s, 1H, −OH); 7.41 (4H, d, $J = 11$ Hz, phenyl); 7.75 (4H, d, $J = 8.4$, phenylsulfonate)	116(2), 124(2), 125(2), 127(2), 146, 151, 155, 161.
4	3.05 (6H, s, Methyl); 7.31 (4H, d, $J = 8.8$ Hz, phenyl); 7.75 (4H, d, $J = 8.5$ Hz, phenyl sulfonate)	110, 122, 123.5, 123.8, 124, 124.9, 125, 127.6, 129, 145, 145.4, 155.8, 157, 159.9.
5	8.21 (2H, s, −OH); 7.57−7.73 (4H, m, phenyl); 8.17 (4H, d, $J = 8.4$ Hz, phenyl sulfonate)	103, 109, 124, 124, 127, 127, 127, 131, 146, 154, 156, 164.
6	5.2 (1H, s, −OH); 8.17 (4H, d, $J = 8.46$ Hz, phenyl sulfonate); 7.18 (3H, m, cresol); 2.35 (3H, m, methyl)	22.5, 115, 122, 122.2, 124.3, 124.7, 124.3, 127.6, 128.8, 142, 147.2, 152.1, 157.7.
7	15.6(1H, s, −OH); 7.28 (4H, d, $J = 9.6$ Hz, phenyl); 6.66−7.91 (6H, m, naphthyl)	117.4, 122.9, 126.7(2), 128, 129, 129.6, 129.9(2), 130.2, 132.4, 133.4, 134.1, 144, 148.4, 180.7.
8	10 (1H, s, −OH); 7.93 (4H, d, $J = 8.16$ Hz, phenyl); 6.83−7.77 (6H, m, naphthyl)	109.7, 115.9, 121.7, 124(2), 126.5, 126.6, 126.8, 127.9, 128.6(2), 129.5, 143.9, 146.3, 157.7, 160.
9	10.5 (1H, s, −OH); 8.09 (4H, d, $J = 8.58$ Hz, phenyl); 7.41 (4H, d, $J = 11.5$, phenol)	116.2(2), 124.4(2), 128(2), 128.6(2), 145.3, 146.3, 157.7, 164.7.
10	3.19 (6H, s, methyl); 8.04 (4H, d, $J = 8.6$ Hz, phenyl); 7.34 (4H, d, $J = 9$, aminobenzene)	40.3, 114.6(2), 123.9(2), 124(2), 128(2), 142.2, 146.3, 151.8, 157.7.
11	10.2 (2H, s, −OH); 8.06 (4H, d, $J = 8.54$ Hz, phenyl); 7.28 (4H, m, resorcinol)	103.9, 108, 117.8, 124(2), 125.8, 128.6(2), 146.5, 153.6, 157.7, 162.1.
12	2.35 (3H, s, methyl); 10.1 (1H, s, −OH), 8.09 (4H, d, $J = 8.4$ Hz, phenyl); 7.33 (4H, m, *p*-resol)	24.3, 116.1, 124(2), 125.1, 126, 128.6(2), 131.3, 132.7, 146.5, 149.2, 157.7.

catalyst by extracting it into acetone and solvent extracts evaporation under vacuum afforded.

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References

[1] (a) Zollinger H. Color chemistry. 3rd ed. Switzerland: Verlag Helvetica Chimica Acta; 2003. p. 165;
(b) Zollinger H. Azo and diazo chemistry, aliphatic and aromatic compounds. London: Interscience Publishers Ltd.; 1961;
(c) Saunders KH, Allen RLM. Aromatic diazo compounds. 3rd ed. London: Edward Arnold (Publishers) Ltd.; 1985.

[2] Clark JH. Chemistry of waste minimization. London: Chapman and Hall; 1995.

[3] Clark JH. Catalysis of organic reactions by supported inorganic reagents. New York: VCH; 1994.

[4] (a) Cornilis A, Laszlo P. Modified clays as efficient acid−base catalyst systems for diazotization and diazo coupling reactions. Synlett 1994;155−61;
(b) Clark JH, Macquarrie DJ. Catalysis of liquid phase organic reactions using chemically modified mesoporous inorganic solids. Chem Commun 1998;853−60;
(c) Clark JH, Macquarrie DJ. Heterogeneous catalysis in liquid phase transformations of importance in the industrial preparation of fine chemicals. Org Process Res Dev 1997;1:149−62;
(d) Bahulayan D, Sukumar R, Sabu KR, Lalithambika M. An easy synthesis of 4,4′-diaminodiphenylmethanes on natural kaolinites. Green Chem 1999;1:191−3;
(e) Choudhary BM, Sateesh M, Lakshmikantam M, Koteesara Rao K, Ramprasad KV, Raghavan KV, Sharma JARP. Selective nitration of aromatic compounds by solid acid catalysis. Chem Commun 2000;25−7;
(f) Samajdar S, Becker FR, Naik BK. Surface-mediated highly efficient regioselective nitration of aromatic compounds by bismuth nitrate. Tetrahedron Lett 2000;41:8017−20;
(g) Bahulayan D, Narayan G, Sreekumar V, Lalithambika M. A mild, efficient, and reusable catalyst reagent system for selective mono nitration and benzylic oxidations. Synth Commun 2002;32:3565−74;
(h) Damodaran B, Litka J, Malathy L. Modified clays as efficient acid−base catalyst systems for diazotization and diazo coupling reactions. Synth Commun 2003;33:863−9;
(i) Renata DS, Rianelli RDS, Souza MCBV, Ferreira VF. Mild diazo transfer reaction catalyzed by modified clays. Synth Commun 2004;34:951−9;
(j) Okada T, Watanabea Y, Ogawa M. Chem Commun 2004;320−1;
(k) Nasreen A. Synlett Spotlight 32. Synlett 2001;8:1341−2;
(l) Muthusamy S, Arulananda Babu S, Gunanathan CV, Jasra R. A new and mild heterogeneous catalytic decomposition of α-diazo carbonyl compounds using montmorillonite or zeolite. Synlett 2002;3:407−10;
(m) Gajare AS, Shaikh NS, Bonde BK, Deshpande VH. Microwave accelerated selective and facile deprotection of allyl esters catalyzed by Montmorillonite K-10. J Chem Soc Perkin Trans 2000;1:639−40.

[5] Dabbagh HA, Mansoori Y. New azoic dyes containing (1H)-tetrazole and azido group. Dyes Pigments 2002;54:37−46.

[6] (a) Fieser LF. Organic syntheses, coll. vol. 2, p. 33, coll. vol. 2, p. 39, vol. 17, p. 9;
(b) Whitlock LR, Siggia S, Smola JE. Anal Chem 1972;44:532;
(c) Rahway NJ. The Merck index. 8th ed. Merck & Co; 1968. The index gives the following reference for details on the synthesis of methyl orange: Gattermann L. Die Praxis des organischen Chemikers. 40th ed. Berlin: de Gruyter & Co; 1961, p. 260−1;
(d) Griffiths J, Mcdarmaid RI. Azide reactive dyes. J Soc Dyers Colour 1997;93:455−9;
(e) Dutta S, Peng Sh-m, Bhattacharya S. Synthesis, structure and redox properties of some 2-(arylazo)-phenolate complexes of rhodium (III). J Chem Soc Dalton Trans 2000;4623−7;
(f) Majumder K, Dutta S, Peng Sh-m, Bhattacharya S. Cyclometallation and N−N bond cleavage of 2-(arylazo) phenols by osmium. Synthesis, structure and redox properties. J Chem Soc Dalton Trans 2001;284−8;
(g) Griffiths J, Mcdarmaid RI. Azide reactive dyes. J Soc Dyers Colour 1978;94:65−70;
(h) Griffiths J, Mcdarmaid RI, Azides. J Soc Dyers Colour 1979;95:13−9.

[7] Dabbagh HA, Mohammad-Salehi J. New transition-state models and kinetics of elimination reactions of tertiary alcohols over aluminum oxide. J Org Chem 1998;63:7619−27.