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Note

Clay catalysed facile rearrangement of diazoaminobenzene to *p*-aminoazobenzene

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Rearrangement of diazoaminobenzene in the presence of acidic cation-exchanged K10-montmorillonite gives exclusively *p*-aminoazobenzene at room temperature within three hours.

Elegant chemistry can be performed with clay and clay supported reagents. Acidic cation-exchanged montmorillonites are efficient solid acid catalysts in a number of acid catalysed reactions[1-4]. They enjoy advantages such as, (a) easy handling, (b) recovery of the catalyst, and (c) greater chemo/regioselectivity etc. In clay supported reagents, the reagents, in general, are deposited on various inorganic solid supports[5]. Pillared clays have larger pore size than many zeolites and hence show the potential for shape selective reactions[6,7] in organic chemistry. In this connection it is pertinent to mention that clay directed aromatic substitutions such as nitrations[8,9], Friedel-Crafts acylation[10] and alkylation[11] have already been reported. Clay catalysed pinacol-pinacolone rearrangement of 1, 2-glycols[12] and Beckmann rearrangement of benzophenone oxime[13] have also been reported.

Our interest[14,15] in utilising clays for achieving selectivity and catalysis in organic reactions prompted us to study the rearrangement of diazominobenzene to *p*-aminoazobenzene.

Diazoaminobenzene (1 g) was thoroughly mixed with an equal or excess amount of K10-montmorillonite or acidic/cation-exchanged clays in a conical flask and kept in the dark for 3/6 hr at room temperature. The mixture was then extracted with ether, the ether layer evaporated and the residue analysed by HPLC. In each case the retention time for the starting material was taken as the internal reference. Rearranged products were identified by co-injection with authentic samples prepared by known methods[16]. The percentage yield and product distribution of these various reactions are presented in Table I.

It could be seen from Table I, that when the reaction was carried out in the presence of natural clays, in addition to the expected *p*-aminoazobenzene, aniline and/or phenol were also formed as byproducts. When the reaction was repeated with acidic/cation-exchanged clays *p*-aminoazobenzene was the exclusive product, except in the case of Cu^{2+} and Ni^{2+} exchanged clays. Greater acidity of cation-exchanged clays leads to the protonation of diazoaminobenzene which then dissociates into diazonium ion and aniline. The diazonium ion thus formed as an intermediate couples at the *para* position of aniline to give *p*-aminoazobenzene (Scheme I). The lower yield of *p*-aminoazobenzene along with the byproduct (may be aniline or phenol; the phenol formed as the diazonium ion could react with the intercalated water) in the last two cases may be due to the low Bronsted acidity of Cu^{2+} and Ni^{2+} exchanged clays[2]. The coupling reactions were also carried out in the presence of other amines viz. *o*-, *m*- and *p*-toluidines with a view to proving the formation of diazonium ion as an intermediate in these reactions (Scheme II, Table II).

From Table II, it is clear that coupling of diazonium ion is more with *m*-toluidine and less with N-methylaniline. In the case of *m*-toluidine the diazonium ion couples at the *para* position with respect to amino function owing to favourable electronic displacement of amino and alkyl groups. Thus, this coupling is highly regioselective. In the

Table I—Percentage yields and product distribution[a] in the rearrangement of diazominobenzene to *p*-aminoazobenzene (PAAB)

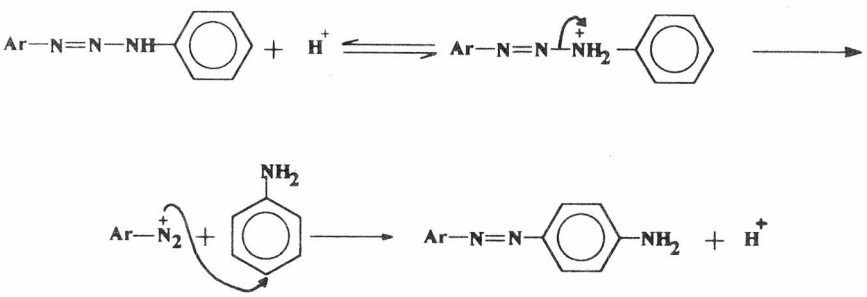
Catalyst (substrate to catalyst ratio)	Reaction Time (hr)	Yield (%)	
		PAAB	Byproduct
K10-mont. (1:1)	3	62	38
K10-mont. (1:1)	6	86	14
K10-mont. (1:2)	3	70	30
K10-mont. (1:2)	6	85	15
K10-mont.-H^+ (1:1)	3	100	—
K10-mont.-Al^{3+} (1:1)	3	100	—
K10-mont.-Fe^{3+} (1:1)	3	100	—
K10-mont.-Cr^{3+} (1:1)	3	100	—
K10-mont.-Cu^{2+} (1:1)	3	82	18
K10-mont.-Cu^{2+} (1:1)	6	88	12
K10-mont.-Ni^{2+} (1:1)	3	71	29
K10-mont.-Ni^{2+} (1:1)	6	81	19

[a]Percentage conversion of substrates to products is 100%.

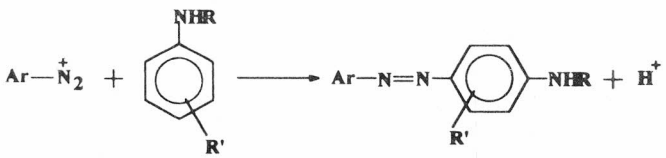
Table II—Product distribution in the coupling reactions

Catalyst	Reaction time (hr)	Conversion (%)	Yield (%)			
			Coupled pdt.	PAAB	DAB	Others*
K10-mont. DAB. *o*-toluidine	3	100	28	5	—	67
K10-mont. DAB. *o*-toluidine	6	100	42	5	—	53
K10-mont. DAB. *p*-toluidine	3	97	28	21	3	48
K10-mont. DAB. *p*-toluidine	6	89	36	21	11	32
K10-mont. DAB. *m*-toluidine	3	100	71	—	—	29
K10-mont. DAB. *m*-toluidine	6	100	73	—	—	27
K10-mont. DAB. NMA	3	100	18	—	—	82
K10-mont. DAB. NMA	6	100	20	—	—	80

*Others could be aniline, phenol and/or coupling component and the individual analysis was not taken.



Scheme I



R = H or CH_3

R = H or o, m or p-CH_3

Scheme II

case of *o*-toluidine, the diazonium ion couples at the *para* position with respect to the amino function which is *meta* to methyl group. Hence, the coupling with *o*-toluidine is not as much as with *m*-toluidine. In the case of *p*-toluidine the *para* position is blocked. So, the coupling of diazonium ion is less as compared with *m*-toluidine and occurs at *ortho* position. In case of N-methylaniline, the diazonium ion may also couple with the N-position of N-methyl function and hence the yields of normal coupled products are less.

It should be noted that diazoaminobenzene when mixed with natural clay and kept in the dark at room temperature for 6 hr, yielded *p*-aminoazobenzene (83%). The same product was obtained in 95% yield when diazoaminobenzene was treated with H^+-exchanged clay for 3 hr.

Thus, the present study highlights the utility of acidic/cation-exchanged clays in the facile conversion of diazoaminobenzene to *p*-aminoazobenzene, apart from exploring its mechanism. The yields of the products obtained by the present

method are much better than those reported by literature procedure[16].

Experimental

K10-montmorillonite (Aldrich), aniline (Sisco-Chem), sodium nitrite (Qualigens), and sodium acetate (Fisher) were used. Diazoaminobenzene and *p*-aminoazobenzene were prepared by known methods[16]. ^{1}H NMR spectra were recorded in a Perkin-Elmer 90 MHz NMR instrument (chemical shifts in δ, ppm) using TMS as the standard and UV spectra on a Jasco (model 7800) UV/Visible spectrophotometer.

Diazoaminobenzene (0.005 mole) was thoroughly mixed with K10-montmorillonite or cation-exchanged clays (1 g). The mixture was taken in a conical flask and kept in the dark for 3/6 hr at room temperature. The mixture was then extracted with ether. Ether layer was evaporated and the residue was analysed by HPLC.

In the coupling reaction, a mixture of K10-montmorillonite (0.2 g), diazoaminobenzene (0.001 mole) and coupling component viz. *o*-, *m*- or *p*-toluidine (0.0018 mole) was thoroughly mixed in a conical flask and was kept in the dark for 3/6 hr at room temperature. The mixture was then extracted with ether. Ether layer was evaporated and the residue analysed by HPLC.

The residue was also purified by column chromatography and the product *p*-aminoazobenzene was recrystallised from aqueous ethanol, m.p. 125°C. Its identity was confirmed by undepressed mixed m.p. with authentic sample[16] and ^{1}H NMR data [δ 4.05 (b, 2H, NH_2), 6.8 (AB quartet, 2H *ortho* to NH_2), 8.0 (AB quartet, 2H *meta* to NH_2), 7.6 to 8.1 (m, 5H, ArH)].

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