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Regiospecific Acylations of Aromatics and Selective Reductions of Azobenzenes over Hydrated Zirconia

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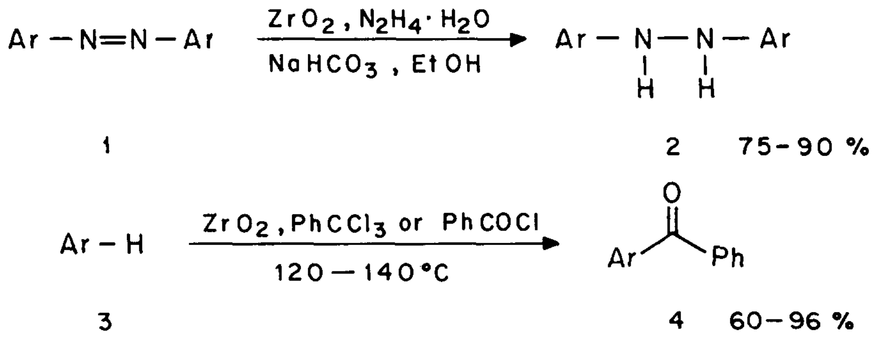
Abstract : *Hydrated zirconia has been found to be an efficient and reusable catalyst for the regiospecific acylations of arenes and selective reductions of azobenzenes to produce benzophenones and hydrazobenzenes respectively.* © 1997 Elsevier Science Ltd.

Benzoylation under Friedel-Crafts acylations is an important unit process for the preparation of many industrially valuable chemicals.[1] However, the use of conventional Lewis acid catalysts e.g. $AlCl_3$ in the homogeneous Friedel - Crafts acylation of arenes entails problems of corrosivity, work up and effluent pollution. Therefore, we have reported[2] recently the use of solid catalysts such as zeolites (e.g. HZSM-5) to replace the traditional Lewis acid catalysts ($AlCl_3$) although the zeolites have failed to benzoylate the less activated arenes such as benzene, naphthalene etc.

The selective reduction of azo compounds to hydrazo derivatives assumes importance because the hydrazo generally suffers a facile reductive cleavage of -NH-NH- bond to amines under the reaction conditions.[3] A variety of reagents such as diimide, $NaBH_4$ in the presence of metal catalysts, LAH, cobalt boride with hydrazine hydrate, SmI_2, hydrogen telluride etc. have been reported[4] to accomplish such azo to hydrazo transformation in good yields. Catalytic hydrogenation[5] has also been used, although further reductive cleavage of the N-N bond can occur. Zn and other metals have also been used for reduction but strongly acidic conditions have to be avoided in order to prevent the benzidine rearrangement of the hydrazobenzenes.



SCHEME 1

Table 1 : Hydrated ZrO_2 - catalyzed transfer hydrogenation of azobenzenes using hydrazine hydrate - $NaHCO_3$[a]

Entry	Substrate	t/h	Products[b] (% Yield)[c]
1	Azobenzene	10	Hydrazobenzene (86)
2	4,4'-Dimethylazobenzene	10	4,4'-Dimethylhydrazobenzene (78)
3	4,4'-Dimethoxyazobenzene	10	4,4'-Dimethoxyhydrazobenzene (80)
4	4,4'-Dichloroazobenzene	10	4,4'-Dichlorohydrazobenzene (90)
5	4-Aminoazobenzene	10	4-Aminohydrazobenzene (75)
6	Azobenzene-4,4'-dicarboxylic acid	10	Hydrazobenzene-4,4'-dicarboxylic acid (81)[d]
7	4-Hydroxyazobenzene	12	Aniline (64) + 4-Aminophenol (36)
8	2-Methoxy-4-hydroxyazobenzene	12	o-Anisidine (62) + 4-Aminophenol (32)
9	1-Phenylazo-2-naphthol	5	Aniline (65) + 1-Amino-2-naphthol (20)
10	1-(4-Methylphenylazo)-2-naphthol	5	p-Toluidine (70) + 1-Amino-2-naphthol (15)
11	1-(4-Methoxyphenylazo)-2-naphthol	5	p-Anisidine (55) + 1-Amino-2-naphthol (33)
12	1-(4-Chlorophenylazo)-2-naphthol	5	4-Chloroaniline (72) + 1-Amino-2-naphthol (23)

a : In the absence of $NaHCO_3$, no reaction took place. b : Characterized by IR, ^1H and ^{13}C NMR and MS. c : Isolated after chromatographic purification. d : The product isolated after acidifying the reaction mixture with acetic acid.

Recent years have witnessed the use of heterogeneous catalysts in liquid phase organic reactions owing to their potential advantages in practical synthesis i.e. the ease of recovery and recycling of the catalyst. For example, attempts have recently been made successfully to use hydrated ZrO_2 as a catalyst for various organic reactions.[6] We wish to report here that hydrated ZrO_2 has been found to be an excellent catalyst for the selective reduction of azoarenes (**1**) to hydrazoarenes (**2**) under transfer hydrogenation conditions as well as the regiospecific benzoylation of arenes (**3**) to benzophenones (**4**) (Scheme 1).

Table 2 : Hydrated ZrO_2 - catalyzed regiospecific acylations of activated arenes in the liquid phase[9]

Entry	Substrate	Acylating agent	Temp. (°C)	Product[a] (% Yield[b])
1	Acetanilide	Acetyl chloride[c]	60	4-Acetylacetanilide (80)
		Benzoyl chloride	120	4-Benzoylacetanilide (71)
2	Aniline	Acetyl chloride[c]	60	4-Acetylacetanilide (65)
3	Anisole	Benzoyl chloride	120	4-Benzoylanisole (65)
		Benzotrichloride	120	4-Benzoylanisole (75)
4	2-Methoxynaphthalene	Acetyl chloride[c]	60	1-Acetyl-2-methoxynaphthalene (60)
		Benzoyl chloride	120	1-Benzoyl-2-methoxynaphthalene (62)
		Benzotrichloride	120	1-Benzoyl-2-methoxynaphthalene (70)
5	Naphthalene	Benzoyl chloride	120	1-Benzoylnaphthalene (80)
		Benzotrichloride	120	1-Benzoylnaphthalene (70)
6	3,5-Dimethoxytoluene	Benzoyl chloride	120	2-Benzoyl 3,5-dimethoxytoluene (80)
		Benzotrichloride	120	2-Benzoyl-3,5-dimethoxytoluene (60)
7	Cyclooctene	Benzoyl chloride	120	1-Cyclooctenylphenyl ketone (62)
8	1-Naphthol	Acetyl chloride[c]	60	1-Naphthylacetate (96)

a : Characterized by IR, ^1H and ^{13}C NMR and MS. b : Isolated after chromatographic purification. c : In the case of acetyl chloride, dichloroethane was used as the solvent; in all other cases, reactions were carried out at 120°C (bath temp.) without solvents.

The catalyst, hydrated zirconium (IV) oxide, was prepared[7] by the treatment of aq. solution of zirconium oxychloride ($ZrOCl_2$ $8H_2O$) with aq. NaOH at RT and was heated at 300°C for 5 h.

Table 1 summarizes the results of various substituted azobenzenes (CH_3, Cl, COOH, NH_2) which underwent selective reduction with hydrazine hydrate to form hydrazo derivatives in high yields.[8] However, it is to be noted that hydroxyazobenzenes underwent reductive cleavage smoothly to produce the corresponding anilines in excellent yields (entries 7-12 of Table 1). Surprisingly, no reaction took place in the absence of base, sodium bicarbonate; at least 2 molar equiv. of $NaHCO_3$ is required to achieve better results. Table 2 shows the regiospecific benzoylation/acetylation of various activated arenes catalyzed by hydrated zirconia.[9] It is remarkable that naphthalene has been benzoylated at the 1-position under the present ZrO_2 conditions in excellent yields. Another notable feature is that even aliphatic olefin could be benzoylated in good yield under the present system (entry 7 of Table 2). In this connection, it should be noted that zeolites have failed to benzoylate naphthalene and cycloalkenes.[2] However, less activated arenes such as benzene, toluene and halobenzenes have failed to undergo benzoylation under the present conditions. The catalyst, hydrated zirconia, was recovered by simple filtration and reused 3 times with no loss of activity and selectivity in all cases studied. Work is in progress to gain further insight into the mechanistic aspect of both the reactions.

In conclusion, we have shown that hydrated ZrO_2 is an excellent, reusable solid catalyst for the selective reduction of azobenzenes and regiospecific benzoylation of activated arenes.

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8. In a typical reaction, a mixture of 4,4'-dichloroazobenzene (1.25 g; 5 mmol), hydrazine hydrate (0.3 g; 5 mmol), $NaHCO_3$ (0.84 g; 10 mmol) and hydrated zirconia (125 mg; 10% by wt) in EtOH (20 ml) was refluxed for 10 h. After the reaction was complete (TLC), the catalyst was filtered off, the reaction mixture concentrated and the product purified by flash chromatography to afford the 4,4'-dichlorohydrazobenzene (1.15 g; 90%). Its spectral data : ^1H NMR (200 MHz, $CDCl_3$) : δ 1.5 (s, 2H), 7.4 (d, J= 9.0 Hz, 4H) and 7.8 (d, J=9.0 Hz, 4H); MS : m/z (% rel. intensity) 252 (M^+, 50), 217 (25), 182 (30), 127 (100) and 90 (60).
9. In a typical reaction, a mixture of cyclooctene (1.1 g; 10 mmol), benzoyl chloride (1.40 g; 10 mmol) and hydrated zirconia (110 mg; 10% by wt.) is heated at 120°C (bath temp.) for 5 h. It was cooled to RT and the catalyst was filtered off. After adding water, the product was extracted with $CHCl_3$ and purified by flash chromatography. Yield : 1.32 g; 62%. Its spectral data : IR (neat) : 3900, 3000, 1770, 1700, 1660, 1590, 1450, 1260, 1200, 990 and 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) : δ 1.03-2 (m, 8H), 2-2.7 (m, 4H), 5.6-5.8 (m, 1H), 7.3-7.6 (m, 3H) and 7.8-8.2 (m, 2H); MS : m/z (% rel. intensity) 214 (M^+, 10), 150 (25), 122 (35), 105 (100) and 77 (80).

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