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Microwave assisted oxidation of *N,N*-Dimethylaniline by using Chromium (VI) Reagents

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Abstract : Chromium (VI) complexes are among the most interesting transition metal complexes that have attracted great attention over the past decades because of their appealing catalyticand oxidizing properties . In the present paper we report the study of products of oxidation of *N,N*-dimethylaniline by ditertiarybutyl chromate in few non aqueous solvents like acetonitrile, tetrahydrofuran and dioxane. The substrate solution and ditertiarybutyl chromate was taken in appropriate ratio, mixed, stirred and irradiated in domestic microwave for the specified periods. The solid products of different colour and compositions so obtained were studied by elemental analysis, FTIR curves and thermogravimetric mass losspattern.

(**Keywords:** *N,N*-Dimethylaniline, Ditertiarybutyl chromate, Dioxane, Tetrahydrofuran)

Introduction

Chromium was discovered in 1798 by the French chemist Vauquelin.[1]It is a transition element located in group VI-B of the periodic table . Chromium (VI)is employed for oxidation of organic compounds and it is redused to lower oxidation states[2].

Oxidations with Cr (VI) is a complex reaction that is influenced by the solvent , structure of the substrate , temperature, acidity of the reaction medium and other factors, hence it is difficult to study from mechanistic point of view. The chemistry of Cr (V) and Cr (IV) as intermediate species , which may be formed during reduction of chromium (VI) attracted many researchers because of their involvement in the mechanism of Cr induced cancers[3].The highly toxic chromium (VI) compounds are converted into environment friendly non-toxic chromium (III) compounds by using several oxidants. *N,N*-Dimethylaniline is a yellowish brown toxic liquid insoluble in water. It is precursor to many commercially important dyes such as malachite green and crystal violet. The oxidation of *N,N*-dimethylaniline by cupric chloride or by chloranil gives *N*-*p*-dimethyl aminobenzyl-*N*-methylaniline, 4,4'-bisdimethylaminodiphenyl methane, crystal violet and methyl violet[4]. The anodic oxidation of *N,N*-dimethylaniline at Pt electrode in acidic buffer leads to *N,N,N',N*'-tetramethylbenzidine[5]. In addition to the electro-oxidative coupling as above, the main oxidation product of *N,N*-dimethylaniline with ring retention is $C_6H_5N(CH_3)_2O$ whereas oxidation with ring degradation may lead to variety of products.

Microwave assisted organic synthesis has grown into a powerful tool in the hands of chemists. Keeping in view, the increasing use of microwave irradiation as a source of clean energy[6], in conformity with the 12 principles of green chemistry[7], the authors have undertaken the oxidation of *N,N*-dimethylaniline with ditertiarybutyl chromate in microwave in non-aqueous solvents. The choice of ditertiarybutyl chromate[8] out of many chromium(VI) based oxidants like Collin's reagent[9], pyridinium chlorochromate[10], pyridinium florochromate[11], tetramethyl ammonium florochromate[12], quinolinium chlorochromate[13]*etc*. is based on its docility accompanied with versatility towards organic substrates. Moreover, the preparation of

ditertiarybutyl chromate is less cumbersome in comparison to the preparation of other variants of chromium (VI). The oxidation products may serve as ligands to form adducts or complexes of chromium in different oxidation states[14,15]. The study of these products may lead to valuable generalizations with regards to the mechanism and other aspects of thereaction.

Experimental :

The chemicals used were all A.R. grade. Only freshly prepared solutions were used. The oxidant was prepared by dissolving crystals of CrO_3 in minimum quantity of tert. Butyl alcohol followed by filtration and decantation to get clear brown solution. Sample-601 was prepared by mixing a solution of 1 g (0.01 mol) of chromium trioxide in 10 mL of tert. butyl alcohol and a solution of 1.2 mL (0.01 mol) of *N,N*-dimethylaniline in 10 mL of acetonitrile as per the requirement for 1:1 oxidant:substrate ratio. The other samples R-602, R-603 were prepared by mixing solution of 0.01 mol of chromium trioxide in tert .butyl alcohol and solution of 0.02 and 0.03 mols of substrate required for 1:2 and 1:3 oxidant:substrate ratio in acetonitrile as solvent for the substrate. Similarly, samples R-604, R-605 and R-605 were prepared by the same procedure using tetrahydrofuran as solvent for substrate and samples R-606 and R-608 in solvent dioxane for the same. In all the cases, the solutions were mixed stirred and then irradiated in LG household microwave oven, MG-3937 C (microwave frequency 2450 MHz) for the period specified in Table 1. The solid products obtained, were washed several times until clear washing before collecting them as solid samples with symbols as above. The estimation of chromium in the products was done volumetrically using $K_2S_2O_8$ (in excess), 0.1 N $K_2Cr_2O_7$ solution and 0.1 N Mohr's salt solution. Elemental analysis of carbon, hydrogen and nitrogen was carried out by Elemental Analyser (Heraeus Vario EL III Carlo Erba 1108). FTIR spectra of the products were recorded on FTIR Spectrophotometer (Shimadzu 8201 PC). TGA was done on Thermal Analysis System (Perkin Elmer Diamond TG/DTA).

Results and Discussion

On the basis of observations as in Table 1 and Table 2, following generalization could be made:

* The reaction is much efficient in acetonitrile as a solvent than either in THF or dioxane. In acetonitrile it takes only 10 sec. as compared to 20 sec. in othercases.
* The products R-607 and R-608, as obtained in case of dioxane as solvent for substrate are almost same except that the number of water molecules is slightly less in case of higher oxidant : substrateratio.
* The oxidation product in all the cases from R-601 to R-608 is *N,N*-dimethylaniline-*N*-oxide which gets associated with reduced chromium to form solidproducts.
* In samples R-601, R-602 and R-603 which are obtained in case of acetonitrile as solvent, chromium has gone to oxidation state as low as II whereas in other cases it is mostly in most stable IIIstate.
* As we go from sample R-601 to R-603, the number of water molecules increases *i.e.* less number of water molecules get associated in the products when the ratio of oxidant is more. This is observed in case of THF and dioxane as solvent aswell.
* The colour of the products in almost all the cases is grey which may be due to charge transfer in the mixed oxide ofchromium.
* As per formulations arrived at, the reaction did not results in any coupling of the rings as reportedearlier[3,4].
* Recrystallization of the products in suitable solvent and the study of the crystals formed may be the further course ofinvestigation.

Table 1. Reactants

Product Code	Substrate	Solvent	Oxidant	Oxidant:Substrate Ratio	Irradiation Time
R-601	DMA	Acetonitrile	TBC	1:1	10 sec
R-602	''	''	''	1:2	10 ''
R-603	''	''	''	1:3	10 ''
R-604	''	THF	''	2:1	20 ''
R-605	''	''	''	1:1	20 ''
R-606	''	''	''	1:2	20 ''
R-607	''	Dioxane	''	2:1	20 ''
R-608	''	''	''	1:1	20 ''

Table 2. Products

Product Code	Colour	Solubility in Water	Empirical Formula	Formulation
R-601	Ash Grey	Insoluble	$Cr_5C_9H_{27}O_{14}N$	$2Cr_2O_3.CrO.HCOOH.C_6H_5N(CH_3)_2O.4H_2O$
R-602	Dark Grey	''	$Cr_5C_8H_{31}O_{17}N$	$2Cr_2O_3.CrO.C_6H_5N(CH_3)_2O.9H_2O$
R-603	Dark Grey	''	$Cr_7C_{10}H_{46}O_{26}N$	$3Cr_2O_3.CrO.C_6H_5N(CH_3)_2O\ 2HCOOH.11H_2O$
R-604	Dark Grey	''	$Cr_6C_{13}H_{39}O_{22}N$	$3Cr_2O_3.C_6H_5N(CH_3)_2O.5HCOOH.2H_2O$
R-605	Ash Grey	''	$Cr_4C_8H_{23}O_{16}N$	$2Cr_2O_3.C_6H_5N(CH_3)_2O.9H_2O$
R-606	Dark Grey	Sparingly Soluble	$Cr_3C_9H_{23}O_{16}N$	$Cr_2O_3.CrO.C_6H_5N(CH_3)_2O.HCOOH.9H_2O$
R-607	Ash Grey	''	$Cr_4C_9H_{27}O_{13}N$	$2Cr_2O_3.C_6H_5N(CH_3)_2O.HCOOH.4H_2O$
R-608	Ash Grey	Insoluble	$Cr_4C_8H_{26}O_{14}N$	$2Cr_2O_3.C_6H_5N(CH_3)_2O.HCOOH.5H_2O$

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