

Scholars Research Library

Archives of Applied Science Research, 2013, 5 (3):134-136 (http://scholarsresearchlibrary.com/archive.html)



Study of ligating ability of oxidation products of diethyl malonate with chromium under heating and microwave irradiation condition

Sangita Katre* and H. O. Pandey**

*Deptt. of Chemistry, Faculty of Science, C. J. Patel Arts, Commerce, Science & Post-graduate College, Tirora, R. T. M. Nagpur University, Maharashtra, India **Deptt. of Chemistry, Faculty of Science, Ranchi University, Ranchi, Jharkhand, India

ABSTRACT

Diethyl malonate (DEM) may be oxidised to degraded and undegraded products like acetic acid, oxalic acid, formic acid, glycolic acid, glyoxal, propanedioic acid etc. In the present work, DEM, in tetrahydrofuran and dioxane as solvents, was treated with ditertiary butyl chromate (TBC) in different molar ratios under ordinary heating and microwave irradiation conditions. The spectroscopic, thermal and other studies of the products formed under different conditions, results in valuable generalizations.

Key words: Diethyl malonate, ditertiary butyl chromate, dioxane, microwave.

INTRODUCTION

The degraded and undegraded oxidation products of DEM as mentioned above may function as ligands under suitable conditions with chromium in different oxidation states with varying ligating ability. TBC has proved to be a versatile oxidant under aqueous and non aqueous media as substantiated by the volume of works done after its first use in 1949 by R.V. Oppenauer and H. Oberrauch¹⁻⁵ .The oxidation of DEM using TBC as an oxidant by conventional method is recently reported ⁶. In the past few decades, Microwave Assisted Organic Synthesis (MAOS) and Microwave Induced Organic Reaction Enhancement (MORE) chemistry gained popularity as a non-conventional eco friendly technique for rapid organic synthesis in conformity with 12 principles of green chemistry⁷. P. Lidstrom et. al.⁸ have reported a detailed survey of MAOS and MORE. Microwave aided oxidation of many organic compounds such as malonic acid has been reported⁹. Highly accelerated rate is the main advantage associated with microwave as the source of energy which enables to carry out syntheses in much less time and with reasonably good yields and ,of course, with remarkable selectivity too. In the present work, DEM as substrate, is taken in THF and dioxane as solvents for oxidation with TBC in different substrate : oxidant molar ratios. The reactions were carried out in domestic microwave oven for the period specified in Table-I. The products were formed very rapidly as compared to ordinary heating and stirring conditions. The nature of the products, thus formed, were studied by elemental, spectroscopic and thermal analysis for their formulation and characterization (Table-II)

MATERIALS AND METHODS

The chemicals used were all A.R grade. The oxidant TBC was prepared by dissolving calculated quantity of pure and dry CrO_3 in tert. butyl alcohol. The clear brown coloured solution obtained by filtration and decantation was used as oxidant. Six samples of DEM solutions in two solvents i.e. dioxane and THF were prepared as per details given in **table -I**. The samples namely, C-1,C-2 and C-3 were prepared by mixing, stirring and heating the solutions in substrate : oxidant molar ratio 1:1, 2:1 and 1:2 respectively, all in solvent THF whereas samples D-1, D-2 and D-3 were prepared by microwave irradiation of the solutions in an LG household microwave oven MG-3937 C (MW frequency 2450 MHz) in substrate : oxidant molar ratio 1:1, 1:2 and 1:2. No solvent was used for the substrate in the preparation of sample D-1 whereas dioxane and THF were used for the preparation of sample D-2 and D-3. The samples were washed thoroughly with acetone until colourless washing and dried before collecting.

The samples were analysed by different experimental methods. Chromium content in the samples was estimated volumetrically whereas carbon and hydrogen were estimated instrumentally by Elemental Analyser-Heraeus Vario EL III Carlo Erba1108. The IR spectra of the samples were recorded on a Fourier Transform Infra Red spectrophotometer Shimadzu 8201PC (4000-400 cm⁻¹). The TG/DT analysis of the products was carried on thermal analysis system- Perkin Elmer. The samples were heated at a rate of 10° C/min. in the temperature range of 25° C to 700° C.

Product Code	Solvent for Substrate	Oxidant	Molar Ratio (S:O)	Reaction Condition
C-1	THF	TBC	1:1	Stirred for an hour
C-2	,,	,,	2:1	Stirred for an hour and left overnight
C-3	,,	,,	1:2	Stirred for an hour and left overnight
D-1		,,	1:1	Microwave 160W, 9 min
D-2	Dioxane	,,	1:2	Microwave 160W, 7 min
D-3	THF	,,	1:2	Microwave 160W, 4 min

Table -I (Reactants)

Table-II	(Products)
I HOIC II	(1 roudeus)

Product Code	Colour	Solubility in Water	Emperical Formula	Formulation
C-1	Deep Brown	Insoluble	$Cr_2C_3H_4O_5$	2CrO.CH ₃ COOH.HCHO
C-2	,,	,,	$Cr_2C_3H_6O_5$	2CrO.CH ₃ COOH.HCHO
C-3	,,	,,	Cr ₆ C ₁₃ H ₁₁ O	
D-1	Blackish	Soluble	$Cr_2C_2H_9O_7$	2CrO.CH ₃ COOH.3H ₂ O
D-2	Dark Brown	Insoluble	$Cr_2C_2H_{12}O_{11}$	2CrO ₂ .CH ₃ COOH.5H ₂ O
D-3	,,	,,	Cr ₄ C ₂ H ₁₅ O ₁₅	2CrO.Cr ₂ O ₃ CH ₃ COOH.8H ₂ O

RESULTS AND DISCUSSION

On the basis of facts compiled in table-I and table-II, we can make many generalizations such as

• The reaction takes place very easily under microwave irradiation conditions. In place of heating and stirring for hours and standing overnight, the products were formed in minutes.

• The reactions are more controlled in dioxane than in tetrahydrofuran as solvent for the substrate.

• The oxidation products are mostly acetic acid which may be the result of degradative oxidation and/or decarboxylation.

• The oxidation state of chromium in almost all the cases is II except in D-3 in which it is in II as well as III state.

• In almost all the cases, the colour of the products was found to be brown which may be due to charge transfer rather than electronic transition.

• The use of solvent is advisable as the oxidation of DEM neat takes more time (D-1) than DEM taken in the form of solution. (D-2 and D-3)

• The formation of water and its subsequent association in the products is observed in case of microwave irradiation as supported by the formulations of D-1, D-2 and D-3

• The products are much cleaner and symmetric in case of microwave irradiation than in case of conventional heating as substantiated by not so reasonable formulation of C-3.

• The extent of oxidation is less in case of conventional heating as supported by the presence of aldehydic fragments in C-1 and C-2. HCHO is quite vulnerable towards oxidation to CO_2 and escape which might be the case in samples obtained by microwave irradiation.

Acknowledgements

The authors are thankful to SAIF, IIT, Mumbai for DTA-TGA analysis and SAIF, CDRI, Lucknow for providing useful data of elemental analysis and FTIR spectrum.

REFERENCES

[1] Oppenaeur, R.V. and Oberrauch, H (Univ. Innsbruck, Austria), Anaus Assoc. Guin-Argentina 37, 246-62, 1949

[2] Suga, T; Kelichkihara and Matsuura, T (University of Hiroshima), Bull. Chem. Soc. Japan, 38, 6,893-6, 1965.

[3] Dupont, G; Dulor, R; Mondou, O. Bull. Chem. Soc. France, 60-1 1953.

[4] Menini, E.; Noryonberski, J.K. (Jessop Hosp. Women, Sheffield, Eng. I) Bio. Chem.J 195-200, 1962.

[5] Mishra, G. D, Sharma, A; Pandey, H. O. J. Chemtracks 10 (1 & 2) 199-200,2008.

[6] Pandey, H. O.; Rasika Singh, Thesis, Ranchi University, Ranchi, 2010.

[7] '*The 12 principles of Green Chemistry*'' United States Environmental Protection Agency. Retrieved, **2006**[8] Lidstrom, P; Tierney, J.; Wathey, B and Westman, J : *Tetrahedron Report No*, 589, 57, 9225-9283, **2001**[9] Katre, S; Gupta, A and Pandey, H.O. : Microwave Aided Oxidation of Malonic Acid by TBC, *J. Chemtracks* 12 (1), 191-94, **2010**