

Environmentally benign synthesis and photochemical reactions of O-Alkyl-S-(3-Phthalyl) Xanthates

K.P.Srivastava*, Sweta Singh and Harimohan Kumar

Department of Chemistry, Ganga Singh College, Chhapra-841 301, Bihar, India.

Abstract

A rapid, efficient and environmentally benign exclusive method of synthesis of O-alkyl-S-(3-phthalyl) xanthates has been developed using reaction of 3-chlorophthalide with potassium-O-alkyl xanthate effectively in an aqueous medium with excellent yields under microwave irradiation. The results were compared with conventional methods. All the ecofriendly synthesized O-alkyl-S-(3-phthalyl) xanthates were characterized by analytical and spectral methods. The photochemical decomposition of O-alkyl-S-(3-phthalyl) xanthates yielded meso-3, 3'-dihydrobipthalide as major product. The mechanisms of the green synthesis and photochemical reactions have also been studied.

Keywords: Green synthesis, microwave irradiation, photochemical reactions, O-alkyl-S-(3-phthalyl) xanthates, meso-3, 3'-dihydrobipthalide

*Corresponding author

1.0 Introduction

Over the past few decades, many significant advances in practical aspects of synthetic organic chemistry have included novel synthetic strategies and methods as well as advent of a vast array of analytical techniques. In these environmentally conscious days, the developments in the technology are directed towards environmentally sound and cleaner procedures. Hence, the present day chemists are no longer confined to using only thermal energy for driving chemical reactions. With increasing complexity of the problems and the availability of newer methods of activation of chemical reactions, chemists have restored to using wide variety of techniques such as photochemical, electrochemical, sonochemical, microwave and enzymatic methods. With easy availability of ultrasound and microwave sources, their use in chemistry has gained momentum recently.

Green chemistry [1-5] revolves around the design, development and implementation of chemical processes and products that reduce or eliminate hazardous substances in a way i.e. feasible and economically viable. That is why it is placed in the frontier areas of chemical research and has been focused for considerable recent research. It is a more eco-friendly green alternative to conventional chemistry practices. It applies not only to the manufacture and use of chemical products- solvents, raw materials and intermediates, but also to the manufacture and use of pharmaceutical and biotech products, consumer and household products and to just about any imaginable article of manufacture or manufacturing process one can name. The chemical and pharmaceutical industries are always under pressure to develop more environmentally friendly organic reaction methodologies. Microwave irradiation, has been shown not

only to reduce reaction times but often to provide higher yields of the desired products as compared to traditional heating methods [6-7]. Therefore, microwave irradiation is used for a variety of organic reactions due to its use in more rapid and cleaner syntheses of organic compounds. All thermally driven reaction can be accelerated by microwave. The spectacular results viz. shorter reaction time, experimental simplicity selectivity of products and easy work up etc. were obtained giving clear indication on the potentialities of this technique over conventional heating. Thus, microwave induced organic synthesis becomes a part of green chemistry. Now-a-days it is also termed as e-chemistry because it is easy, economic, effective and eco-friendly.

2.0 Materials and methos

Materials and Techniques

All starting reagents were purchased from commercial sources and used without further purification. 3-chlorophthalide, 3-bromophthalide, K-O-ethyl xanthate, K-O-propyl xanthate, K-O-n-butyl xanthate, etc. were prepared by reported standard procedures [8-10]. The microwave irradiations were performed using a commercial / kitchen microwave oven model BMO: 700T (BPL-make). All irradiation experiments were carried out using a non-rotating annular photochemical reactor. All melting points were determined on a melting point apparatus and are uncorrected. Infrared (KBr) spectra were recorded on a Perkin-Elmer, Model-137 infrared spectrophotometer and UV spectra were determined on a Beckmann-DB spectrophotometer. NMR spectra were recorded on a Bruker Varian-300 MHz NMR spectrometer in CDCl_3 with TMS as an internal standard. The chemical shifts are expressed in δ -scale downfield from TMS and proton signals are indicated as s =

singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The TLC was run on silica gel plates using acetone-benzene (1:3) as the irrigant. All compounds were analysed satisfactorily for C, H, S and N using Carl-Ebra 1106 elemental analyser in micro analytical laboratory.

Synthesis of O-alkyl-S-(3-phthalyl) xanthates

A solution of 3-chlorophthalide in acetone, maintained around 298K was

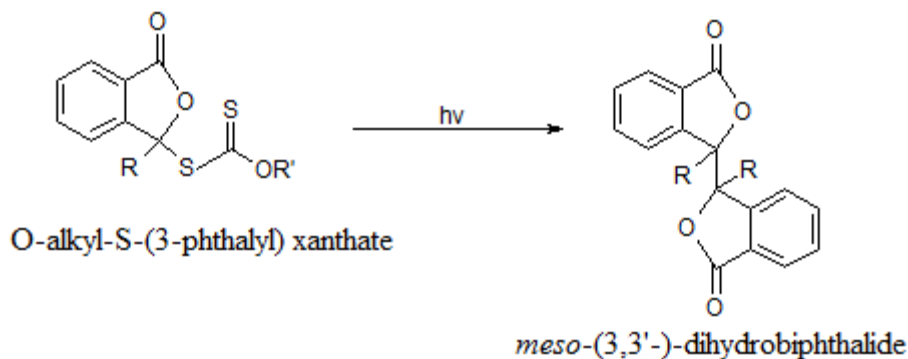
gradually added to potassium-O-alkyl xanthate in small portions and with constant stirring in microwave oven. After removal of the solvent from the reaction mixture, the residue was treated with excess of water to remove any unchanged potassium-O-alkyl xanthate and recrystallized from a mixture (1:1) of ethanol and methylene chloride to give O-alkyl-S-(3-phthalyl) xanthates (1) (Scheme-1).



Scheme-1: Synthesis of O-alkyl-S-(3-phthalyl) xanthates

Photolysis of O-alkyl-S-(3-phthalyl) xanthates

A solution of O-alkyl-S-(3-phthalyl) xanthate (3) in benzene was irradiated for 30 minutes at room temperature. The removal of the solvent under vacuum gave a product which on treatment with a small quantity of acetone gave meso-3, 3'-dihydrobipthalide m.p. 543K, on crystallization from acetic acid (Scheme-2).



Scheme-2: Photolysis of O-alkyl-S-(3-phthalyl) xanthates

3.0 Results and discussion

In the present investigation, we have examined the reactions of a few monohalophthalides with potassium O-alkyl

xanthates, with a view to examining the nature of the products formed in these reactions. Treatment of potassium O-ethyl xanthate with an acetone solution of 3-

chlorophthalide gave a product which was identified as O-ethyl S-(phthalyl) xanthate (1a), m.p. 380K. The identity of this product was confirmed on the basis of analytical results and spectral data. The IR spectrum of 1a showed carbonyl absorption at 1770 cm characteristic of a γ -lactone. The MNR spectrum of 1a (Figure-1) showed a multiplet centered around 7.9 ppm (5H) due to the four aromatic protons and one tertiary proton attached to the 3-position of the phthalide nucleus. In addition, the spectrum showed a quartet centered around 4.89 ppm (2H) due to the methylene protons and a triplet at 1.42 ppm (3H) due to the methyl protons or the alkyl side. The formation of 1a may be rationalized in terms of a direct displacement of the chloride ion as shown in Scheme-3. The reaction is proceeding through the formation of the intermediate aldehydoxanthate, which can then rearranged to 1a through a bicycle-[3,2,1]-transition state [11].

With a view to finding out whether, the intermediate is formed in the reaction or not, we have examined the absorption spectrum of the product mixture, immediately after mixing together the 3-chlorophthalide and potassium O-ethyl xanthate in a 1:1 ratio, in acetone solution around 278K. The absorption spectrum of this mixture was characterized by the presence of an absorption maximum at 390 nm (ϵ , 80), characteristic of acyl and aroyl xanthates containing the -CO-S-CO- chromophore. These observations support the view that the reaction of 3-chlorophthalide with potassium O-ethyl xanthate proceeds through path as shown in Scheme 3.3. Similarly the reactions of potassium-O-n-propyl xanthate and potassium-O-n-butyl xanthate with 3-bromophthalide resulted in the formation of O-n-propyl S-(3-phthalyl)xanthate 1b and O-n-butyl S-(3-phthalyl)xanthate 1c in 95% and 93% yields respectively (Scheme-3).

Analytical and Spectral Characterisation of O-ethyl S-(3-phthalyl) xanthate (1a)

Analytical Data (C,H, S %): calculated -51.96, 03.93, 25.19. Found-51.98 ,03.86, 25.30

IR Spectrum (KBr) [ν_{\max}] = 1770 cm^{-1} (γ -lactone, C=O group) and 1040 cm^{-1} (C=S).

UV Spectrum (CH_2Cl_2) [λ_{\max}] = 278nm, (ϵ , 12,600) and 362nm, (ϵ , 50).

Analytical and Spectral Characterisation of O-n-propyl S-(3-phthalyl) xanthate (1b)

Analytical Data(C,H, S %): calculated-53.75, 04.47, 24.24. Found-53.80, 04.56, 24.30.

IR Spectrum (KBr) [ν_{\max}] = 1770 cm^{-1} (γ -lactone, C=O group) and 1050 cm^{-1} (C=S).

UV Spectrum (CH_2Cl_2) [λ_{\max}] = 278nm, (ϵ , 12,800) and 364nm, (ϵ , 50).

Analytical and Spectral Characterisation of O-n-butyl S-(3-phthalyl) xanthate (1c)

Analytical Data(C,H, S %): 55.31,04.96,22.69.Found- 55.18,04.86,22.50.

IR Spectrum (KBr) [ν_{\max}] = 1765 cm^{-1} (γ -lactone, C=O group) and 1040 cm^{-1} (C=S).

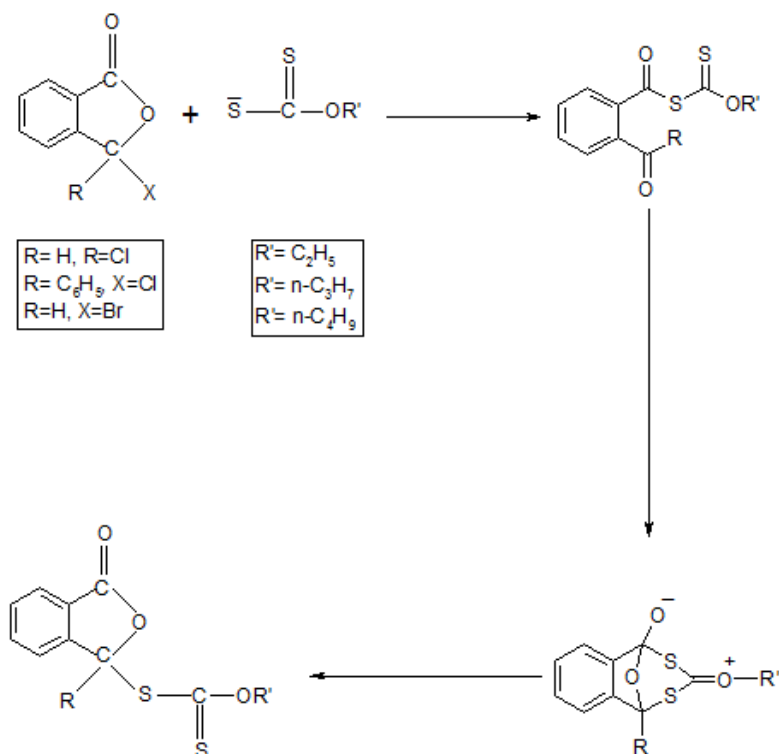
UV Spectrum (CH_2Cl_2) [λ_{\max}] = 278nm, (ϵ , 15,850) and 364nm, (ϵ , 130).

Analytical results & Spectral Characterization of meso-3, 3' dihydrobipthalide

Analytical Data(C,H, %):calculated: 72.18, 03.76. Found-72.25,03.90.

IR Spectrum (KBr) [ν_{\max}] = 1765 cm^{-1} (due to γ -lactone i.e. C = O group).

UV Spectrum (CH₂Cl₂) [λ_{\max}] = 238 nm, (ϵ , 1350), 276 nm, (ϵ , 3600), 284nm (ϵ , 3,750), 296 nm (900), 308 nm (900), 362 nm (2050), 376 nm (1680) and 384 nm (1450).



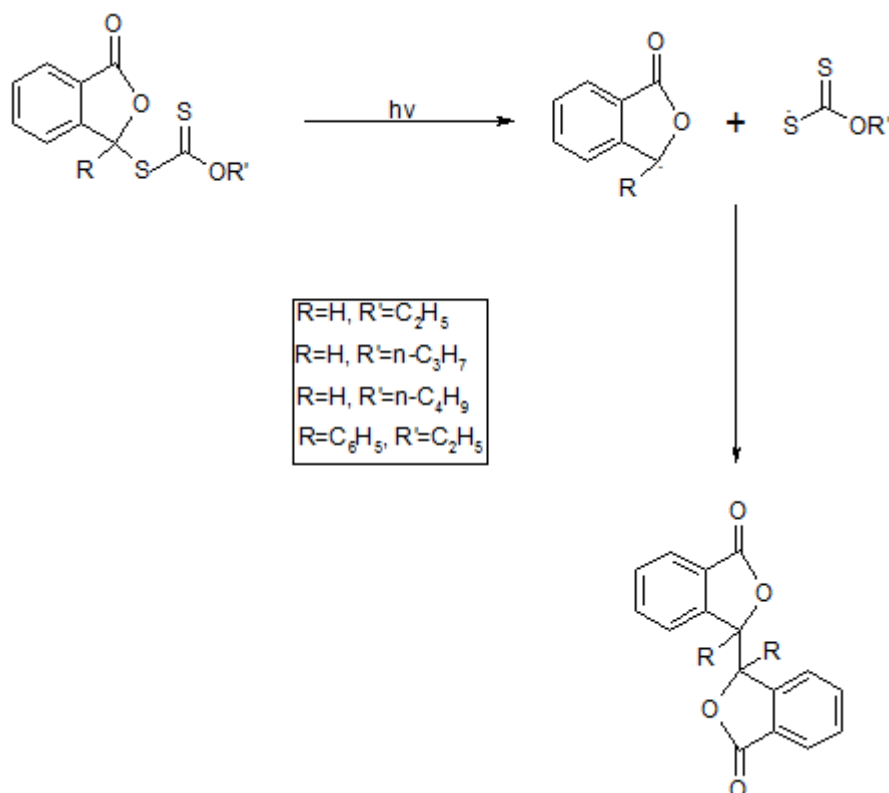
Scheme-3: Mechanism of synthesis of O-alkyl-S-(3-phthalyl) xanthates

Compound	M.P (in K)	% Yields	
		Classical method	Green method
1a	381	80	92
1b	365	74	93
1c	363	76	89

Table-1: Comparison of % yield of synthesized compounds

Compound	% Yield
1a	25
1b	20
1c	35

Table-2: The % yield of photolysed compounds



Scheme-4: Mechanism of photolysis of O-alkyl-S-(3-phthalyl) xanthates

The thermal transformations of unsymmetrical phthaloyl dixanthates and phthalic bis-amine dithiocarbamic anhydrides have been reported earlier. In the present investigation, we have examined the photochemical transformations of several O-alkyl-S-(3-phthalyl) xanthates with a view to studying the mode of these reactions. Photolysis of O-ethyl S-(3-phthalyl) xanthate (1a) in benzene solution at room temperature gave a 25% yield of meso-3, 3'- dihydrobipthalide, m.p. 543K, as the only isolable product. Under analogous conditions, the photolysis of O-n-propyl S-(3-phthalyl) xanthate (1b) and O-n-

butyl S-(3- phthalyl) xanthate (1c) gave meso-3,3'- dihydrobipthalide in 20% and 35% yields, respectively. The formation of meso-dihydrobipthalide in the photolysis of O-alkyl-S-(3-phthalyl) xanthates suggests that the photo-fragmentation reactions may be proceeding through the initial fission of a C-S bond, leading to the formation of the phthalide radical, which then dimerizes to meso-dihydrobipthalide as shown in Scheme-4. A similar type of photochemical fragmentation of the C-S bond is reported in the case of unsymmetrical phthaloyl dixanthates and 9, 9—dixanthogenyl xanthene [12].

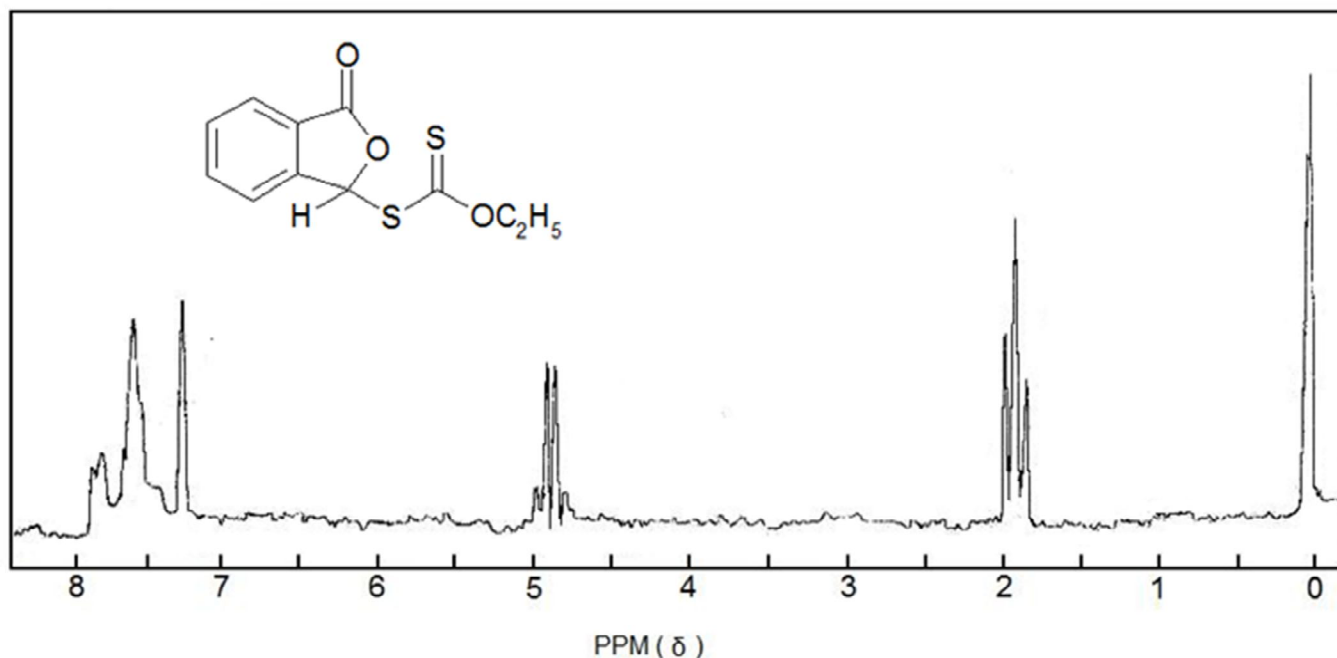


Figure-1: NMR spectrum of O-ethyl S-(phthalyl) xanthate (1a)

4.0 Conclusion

In the present protocol we observed better yields in a shorter period compared to the conventional methods. In conclusion, we have described here an efficient and environmentally benign synthesis of O-alkyl-S-(3-phthalyl) xanthates and their photochemical reactions under microwave irradiation which is simple, mild and

ecofriendly from green chemistry point of view. The photochemical decomposition of O-alkyl-S-(3-phthalyl) xanthates yielded meso-3, 3'-dihydrobiphtalide as major product. The mechanisms of the green synthesis and photochemical reactions have also been presented.

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