

# An Alternate Route for One-pot Synthesis of Poly (Methylene-bis) - 1, 3 -Indandione

N.D. Zargar\*, K.Z Khan

Department of Chemistry, University of Kashmir, Srinagar (J&K), India

\*Corresponding author: nded.1092@rediffmail.com

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**Abstract** Dimethyl sulphoxide reagent brings about N-methyl thiomethylation and N-hydroxy methylation in phthalimide at elevated temperature. It also converts 5,5-disubstituted barbituric acid to its N-methyl thiomethyl and N,N'-methyl thiomethyl derivatives at reflux temperature. A convenient and efficient procedure for the synthesis of poly(methylene-bis)-1,3-indandione derivative (2) was developed by one-pot reaction of 1,3-indandione (1) when refluxed with DMSO at 180 °C. This provides an alternate method of mechanistic interest for the synthesis of tetrad (2) with excellent yield. The condensation product (2) can act as a basic unit for the synthesis of a polymer.

**Keywords:** DMSO, indandione, tetrad, poly (methylene-bis), phthalimide, barbituric acid

## 1. Introduction

Dimethyl sulphoxide apart from being used as a polar aprotic solvent has also been used as a versatile reagent. It has been employed successfully to bring methyl thiomethylation, methylene insertion and ylide formation in different substrates at elevated temperature [1,2,3,4]. It converts 1,6-naphtharidene an analogue of 4-hydroxy coumarin to dinaphtharidinyl methane at reflux temp. and brings about N-methyl thiomethylation and N,N'-methyl-thiomethylation in 5,5-disubstituted barbituric acid. This versatile reagent as in case of 4-acetoxy coumarines [5] converts oxazonones to the corresponding ylide [6]. DMSO has also been used to bring about thermal dehydration and dethioacetalisation of  $\beta$ -hydroxy dithioacetals to yield  $\alpha, \beta$ -unsaturated aldehydes [7] and  $I_2/H_2SO_4/DMSO$  reagent for affecting cyclizations of 2-hydroxy chalcones [8].

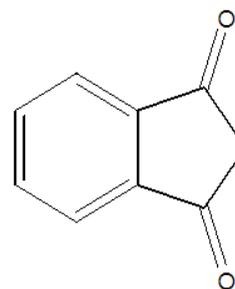
Keeping this in mind it was decided to expose 1,3-indandione containing acidic hydrogens to dimethyl sulphoxide, the oxygen of which can be protonated at elevated temperature.

## 2. Results and Discussion

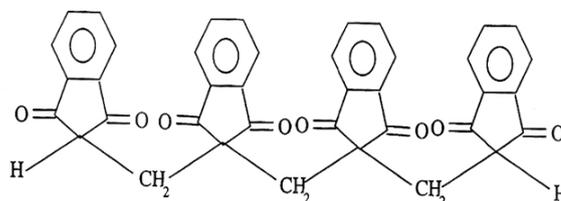
1,3-indandione, an important member of class of  $\beta$  diketones has been used as a substrate in different reactions giving a variety of products of mechanistic and chemical interest [9-16]. When refluxed with DMSO at ~180 °C for 5 hours and work up through addition of water afforded a single pale yellow colored solid which did not melt even when heated up to 355 °C. The compound showed negative test for sulphur.

The mass spectrum of the compound was not recorded because of its high melting nature; however, elemental analysis is in full agreement with molecular formula

$C_{39}H_{24}O_8$  assigned to it. This indicates participation of 4-indandione nuclei in it. The remaining three carbon atoms must have been derived from DMSO most likely in the form of methylene groups. The compound was assigned structure (2) which is similar to the one obtained upon interaction between 1,3 indandione and formaldehyde [17].



(1)



(2)

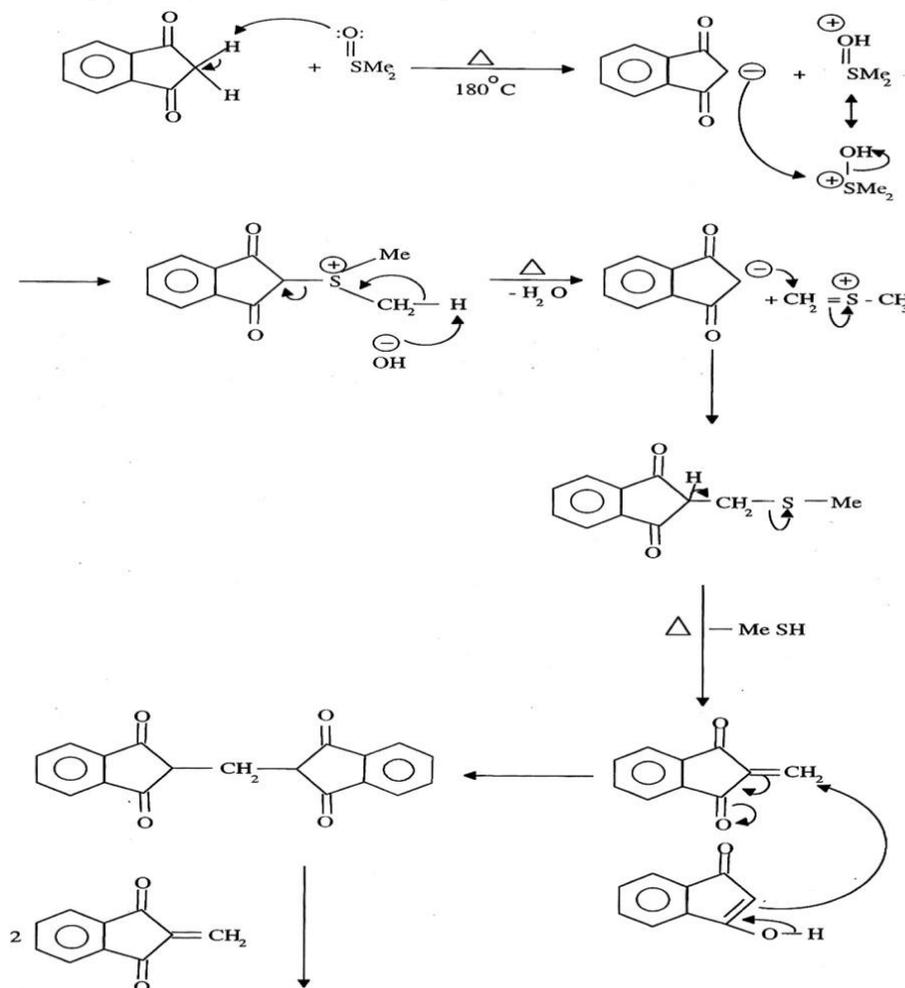
The  $^1H$  NMR spectrum of the compound recorded with difficulty in the mixture of  $CDCl_3$  and  $DMSO-d_6$  shows a sharp singlet equivalent to two protons at  $\delta$  8.26 which is assigned to the two terminal methine protons. Apart from the multiplet spread over the aromatic region the spectrum shows two singlets at  $\delta$  1.23 and 2.09 equivalent to four and

two protons respectively. The former was assigned to the two terminal methylene protons and latter to the central methylene protons.

The ir spectrum of the compound shows only one strong carbonyl band at  $1710\text{cm}^{-1}$  which is at right value for the carbonyls of 2-substituted indandione.

Formation of this compound from DMSO alone can be explained on the basis that 1,3-indandione, being sufficiently acidic probably manages to protonate the oxygen of DMSO at higher temperatures. The resulting

sulphonium species is then attacked by the carbanion resulting in the formation of 2-methyl thiomethyl 1,3-indandione which may not survive at higher temperature and should suffer loss of thiomethanol. The resulting species can interact with another molecule of 1,3-indandione to give 2,2-methylene -bis 1,3-indandione, which reacts further in the same way with two more indandione molecules and ultimately gives (2).Scheme-1.



(2)(Scheme -1)

## 2.1. Spectral Data of (2)

$^1\text{HNMR}$	( $\delta$ ) $\text{CDCl}_3/\text{DMSO-d}_6$
1.23	(4H, s, $\text{CH}_2$ terminal)
2.09	(2H, s, $\text{CH}_2$ central proton)
8.26	(2H, s, CH terminal)
7.81-8.10	(m, spread over the aromatic region)
$\gamma_{\text{max}}$ (KBr)	1710 (strong) and $1607\text{cm}^{-1}$

## 2.2. Experimental

A mixture of 1,3 indandione (1g) and DMSO (10ml) was refluxed at  $\sim 180^\circ\text{C}$  for 5 hours. Preliminary tlc monitoring shows transformation. Reaction mixture was cooled and diluted with water. Precipitate results, which was filtered and washed several times with water. A yellow colored single compound labeled as (2) in high yields (80%) was obtained. It is soluble in DMSO and did not melt up to  $355^\circ\text{C}$ . Sulphur was found to be absent.

## 3. General Information

Melting points were taken on a Tempo block melting point apparatus and are uncorrected. DMSO used as a reagent was carefully dried according to the standard procedure. All the solvents used were of AR grade. Spectral data of the compound was recorded in RSIC Punjab University Chandigarh India.

## 4. Conclusion

Poly (methylene-bis) 1, 3-indandione has been synthesized from the parent compound 1, 3-indandione using DMSO as an appropriate reagent. The tetrad (2) obtained by one pot reaction procedure undergoes various characterizations using solubility, melting point, chromatography, solvent separation techniques, crystallization,  $^1\text{HNMR}$ , ir

spectroscopy and elemental analysis. Silica gel acts as an excellent adsorbent. The combined results of physical and spectroscopic studies confirmed the formation of tetramer (2).

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