

Synthesis of Unusual Trimers in 1,3-Indandione

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Abstract

Dimethyl Sulphoxide-acetic anhydride reagent converts 1,3-indandione to the ylide (2) and a much awaited dimer (3) at room temperature. However , when 1,3-indandione was interacted with pre- heated DMSO-acetic anhydride at waterbath temperature it affords an unusual trimer (4) and a novel compound (5), methine-tris-1,3-indandione along with the ylide (2)

Key words

DMSO, Acetic anhydride, Indandione, Ylide Trimer.

General information

Melting points were taken on a Tempo block and are uncorrected. Spectral data of the compounds was recorded in RSIC Punjab university India.

Materials

DMSO was carefully dried according to the standard procedure. All the solvents used were of AR grade

Introduction

Dimethyl sulphoxide acetic anhydride, a versatile reagent has been a subject of reviews¹⁻⁵ with a wide range of chemical applications. It brings about oxidation of secondary alcohols⁶, oxidative - rearrangements⁷, formation of methylene- bis-adducts, oxidative degradation and oxidative cyclisations in different β -diketones depending upon the reaction conditions and structure of the diketone . This reagent also converts 4-hydroxy coumarins and its substituted derivatives , under varying conditions , to a variety of products of both mechanistic and chemical- interest^{8,9}.

In view of this it was considered to investigate the reactions of 1, 3-indandione with DMSO- acetic anhydride under different conditions.

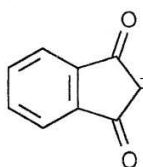
Experimental

A mixture of DMSO(16ml) and acetic anhydride(8ml) was heated at water bath temperature for two hours. Then 2 grams of 1,3-indandione was added to it and the reaction mixture was kept on a boiling water bath for 12 hours. Tlc monitoring indicated formation of a number of products. Removal of solvent under reduced pressure afforded a red colored solid which upon column chromatography over silica gel using benzene ethyl- acetate(70:30) as eluent yielded the ylide(2) in smaller

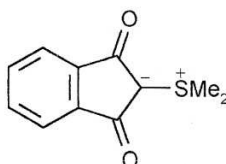
amounts along with another compound (4), m.p.265-270⁰C , soluble in chloroform and a light brown coloured compound (5) in good yields. It was soloube in chloroform and did not melt upto 355⁰C.

Results and Discussion

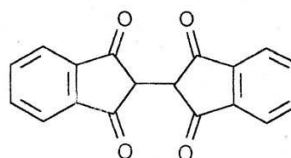
1,3-indandione is an important member of class of 1,3-diketo compounds and literature is full of references giving its reactions with a variety of substrates yielding a wide range of compounds of pharmaceutical interest. Its reaction with DMSO-acetic anhydride has been found to result the corresponding ylid (2) in good yields ¹⁰ and a dimer (3) at room temperature.



(1)

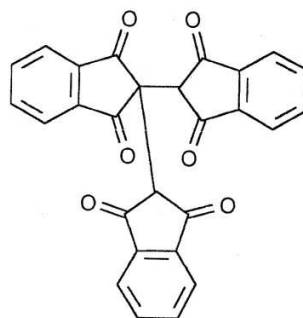


(2)



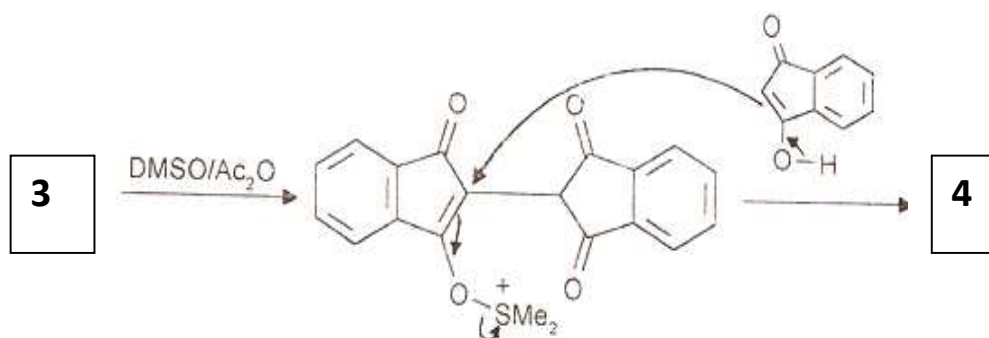
(3)

The pre heated 2:1 (v/v) mixture of DMSO and acetic anhydride has been found to furnish formaldehyde in situ which reacts with 1,3-dicarbonyl compounds to give their corresponding 2,2'-methylene- bis- derivatives. Interaction of this modified reagent with 1,3-indandione at waterbath temperature and workup of the reaction mixture followed by chromatography of the residue obtained, yielded surprisingly the ylide (2) in minimal amounts and an unusual trimer, m.p. 265-70⁰C , did not respond positively when tested for the presence of sulphur and was found to have the molecular formula C₂₇H₁₄O₆ on the basis of elemental analysis and mass spectrum showing molecular ion at m/z 434. This immediately suggested condensation of three molecules of 1,3-indandione without the involvement of formaldehyde, generated from the modified reagent. The pmr spectrum of this compound showed the presence of two methine protons and twelve aromatic protons at δ 2.69 and 7.3 to 8.5 respectively. Along with these, the infra red spectrum showing a broad carbonyl band centered at 1700cm⁻¹ was also suggestive of the structure (4)

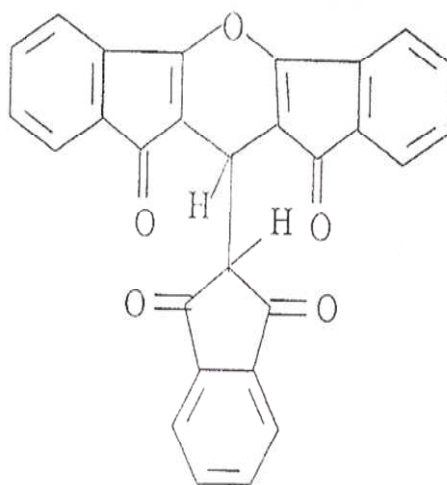


(4)

DMSO and acetic anhydride in the initial stages does produce $(\text{CH}_3)_2\text{S}^+-\text{OAc}$ and O^-Ac and the formation of dimer (3) and from it that of trimer (4) can be rationalized as depicted below



The other novel compound (5), identified from this reaction was methine- tris- 1,3-indandione . It did not respond positively when tested for the presence of sulphur and could not melt up to 355°C, therefore its mass spectrum could not be recorded . However, on the basis of elemental analysis ,its molecular formula was found to be $\text{C}_{28}\text{H}_{14}\text{O}_5$ which involves participation of three indandione residues and one carbon most likely from formaldehyde generated in situ in the formation of this compound. This molecular formula indicates that the trimer once formed might have suffered dehydration under reaction conditions to give the compound which can safely be assigned the structure (5)

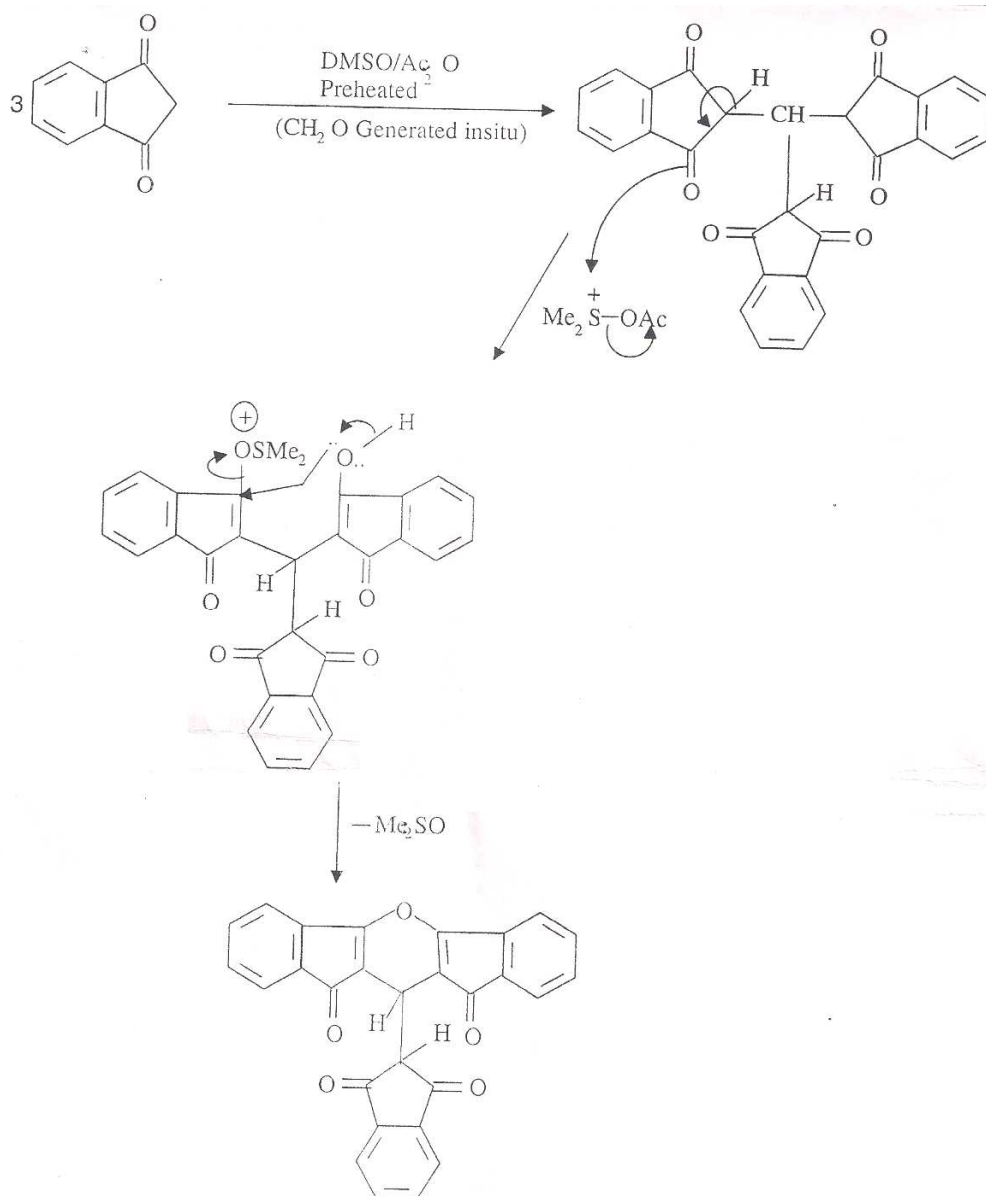


(5)

The ir spectrum of this compound showing doublet of carbonyl band at 1750 and 1692 cm^{-1} is in full agreement with this structure. These bands can be assigned to the carbonyls of 2-substituted indandione residue and the two α,β -unsaturated five membered cyclic ketones respectively. Apart from this carbon -carbon double bond stretching band at 1652 cm^{-1} is also in favour of this structure.

The pmr spectrum of this compound shows a multiplet equivalent to 12 protons in the aromatic region between δ 6.69 to 8.75. Apart from this, it shows two doublets at δ 2.1 and 3.2 equivalent to one proton each. The doublet at up field value can be assigned to the proton which is doubly allylic and the other at downfield to the methine proton flanked on either side by carbonyl groups.

Formation of methylene- bis-derivatives and cyclisations involving dehydration have been observed during reactions of β -diketones with DMSO-acetic anhydride but formation of methine- tris- derivative is being observed for the first time (scheme- I)



Spectral data

(4) $^1\text{H NMR}$ (δ)

($\text{CDCl}_3/\text{TFFA}$)

2.69 (2H,s ,-CH), 7.3 to 8.5 (12H,m,Ar-H)

Y_{max} (KBr)

1700 (broad), 1610,1450 and 1258 cm^{-1}

Mass

m/z 434 (M^+), 301, 302, 288, 146. 105 (base peak), 104, 77 and 76

(5) $^1\text{H NMR}$ (δ) (CDCl_3)

2.1 (1H, d,-CH-),3.2 (1H,d,-CH-),6.69-8.75 (12H,m,Ar-H)

Y_{max} (KBr)

1715, 1692 and 1652 cm^{-1}

Acknowledgement

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