Research Article

Synthesis and Spectral Characterization of Novel Spiroindan-1,3-Dione: A Diels Alder Adduct

N. D. Zargar and K. Z. Khan

Department of Chemistry, University of Kashmir, Srinagar, 190006 Jammu and Kashmir, India

Correspondence should be addressed to N. D. Zargar; nded.1092@rediffmail.com

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DMSO/Ac₂O reagent converts 1,3-indandione (**1**) to an unusual dimer 1H,1'H-2,2'-biindene-1,1',3,3' (2H,2'H) tetrone and a dimeric condensation product along with an ylide (**1a**) at room temperature. This reagent also brings about oxidation of secondary alcohols to corresponding ketones, methyl thiomethylation, and N-hydroxymethylation in phthalimide and converts 4-hydroxycoumarins and dicoumarol to different oxidative and degradation products under varying conditions. However, when 1,3-indandione was refluxed with DMSO/Ac₂O reagent at 150°C, it afforded a novel compound, 2-spiroindan 1,3-dione (**2**), a Diels Alder Adduct, analogous to (**3**) obtained upon treatment of 1,3-indandione with formaldehyde in presence of primary amines.

1. Introduction

Dimethyl sulfoxide, a polar aprotic liquid, has been used in combination with a number of activators but the most important and extensively used was acetic anhydride. DMSO-acetic anhydride reagent has been a subject of monographs. It brings about oxidative rearrangements [1], oxidative degradation, oxidation of secondary alcohols [2], and methyl thiomethylates -OH group in different sugar units [3]. Interaction of this reagent with 4-hydroxy coumarins and 3-substituted 4-hydroxy coumarins results in a wide range of products under varying conditions both of mechanistic and pharmacological interests [4].

1,3-Indandione, a member of class of 1,3-diketo compounds has been found to yield a number of compounds with different substrates having marked chemical and biological activities. Its interaction with 5-bromo furfural in ethanol gives 5-bromo furfuryl diindandionyl-methane [5]. It reacts with cyclic ketones such as cyclopentanone and cyclohexanone to give the corresponding 2-cycloalkylidene-1,3-indandione [6]. 1,3-Indandione also reacts with indazole-dione and furnishes a condensation product [7].

3-Substituted-1,3-indandione shows Michael addition reaction with β -nitro vinyl benzene to give an adduct having fungicidal property which depends upon the type

and location of the substituent on aryl residue [8]. In a double Michael addition reaction 1,3-indandione has been found to interact with 1,5-diphenyl-pentadiene-3-one in a (-) quinone catalyzed stereo-specific reaction to give optically active trans-spiran [9]. 1,3-Indandione also undergoes condensation reaction with aromatic aldehydes to give 2-arylidine-1,3-indandione [10]. Reaction of 1,3-indandione with active methylene compounds such as malononitrile has been found to give a number of compounds [11]. Its condensation with heteroatom carbaldehydes has been found to give 2-alkylidenes which undergo Michael addition of 1,3-indandione to yield a 2:1 adduct [12]. Inter- and intramolecular C-H...O bonding have also been observed in the anions of 1,3-indandione derivatives [13].

Keeping in view it was thought better to interact 1,3-indandione with DMSO-acetic anhydride reagent at elevated temperature (~150°C) as the former contains active hydrogens which can protonate the oxygen of DMSO and set the reaction in motion.

2. Experimental

2.1. General Comments. Solvents purchased from Merck were of AR grade. 1,3-Indandione was received from Guide Chem. DMSO was carefully dried according to the standard

FIGURE 1: Substrate I, 3-indandione. (1a) Ylide.

FIGURE 2: Novel compound 2-spiroindan 1,3-dione.

procedure [14]. All reactions were monitored by TLC plates precoated with Silica gel Si₆₀ F₂₅₄ from Merck. Melting points were recorded on Tempo block melting point apparatus and are uncorrected. IR spectra were recorded on Perkin Elmer spectrophotometer of the range 4000–400 cm⁻¹. ¹HNMR was recorded on 300 MHz Bruker instrument. Mass was recorded on Jeol mass spectrometer in electron ionization mode. Ylide (1a) was synthesized by the earlier reported method [15].

2.2. 2-Spiroindan-1,3-Dione. A mixture of 1,3-indandione (1g), DMSO (16 mL), and acetic anhydride (8 mL) was maintained at ~150°C in an oil bath for eight hours. TLC monitoring indicated formation of a mixture of products. The reaction mixture was cooled, diluted with excess of water, and extracted with ether. The ether layer was washed several times with water and dried over anhydrous sodium sulphate and removal of solvent afforded a gummy residue, column chromatography of which over silica gel gave only one pure product in good yields m.p. 244–246°C. The compound was found to be devoid of sulphur:

Ylide (1a), yield (52.5%), m.p. 165°C ¹HNMR CDCl₃, 300 MHz, (δ), ppm,

3.024 (6H, s, S⁺ (CH₃)₂), 7.760–7.946 (4H, m, Ar-H)

$\nu_{\max}$ (KBr) cm⁻¹ 1635 and 1595 cm⁻¹,

2-Spiroindan 1,3-dione (2) yield (59%), M.P. 244–246°C, ¹HNMR DMSO-d₆, 300 MHz, δ, ppm,

2.48 (2H, s, =C–CH₂–C–), 3.34 (2H, s, O–CH₂–C–) 7.02–7.97 (8H, m, Ar-H),

$\nu_{\max}$ (KBr) cm⁻¹ 1710 (shoulder) 1700, 1570, 1400, 1340, and 1230 cm⁻¹,

Mass M⁺ (*m/z*) 316, 288, 158, and 76.

R = Allyl, Aryl

FIGURE 3: Analogous Spiro compound of (2).

3. Results and Discussion

The reaction between 1,3-indandione and DMSO/Ac₂O reagent at room temperature has been found to afford an unusual dimer 1H,1'H-2,2'-biindene-1,1',3,3'(2H,2'H)-tetrone, a dimeric condensation product along with an ylide (1a) in better yields than those reported earlier [15]. However, when 1,3-indandione was refluxed with this versatile reagent at 150°C (±5°C), the reaction proved to be destructive; that is, instead of two enantiomers TLC monitoring indicated the formation of a number of products which could not be resolved. Workup of the reaction mixture and chromatography of the material resulted in only one pure compound m.p. 244–246°C and was found to be devoid of sulphur. On the basis of elemental analysis and mass spectrum showing M⁺ at *m/z* 316, its molecular formula was found to be C₂₀H₁₂O₄ and the structure ultimately assigned to this compound is (2) (Figures 1 and 2).

The ¹HNMR spectrum of this compound was extremely simple showing two singlets equivalent to two protons each at δ 2.48 and 3.34 and a multiplet equivalent to eight protons in the aromatic region at δ 7.20–7.97. This suggests involvement of two indandione molecules and two methylene groups most certainly derived from DMSO in the formation of this compound. The structure (2) assigned to this compound is also supported by its IR spectrum showing strong carbonyl bands at 1700 and 1710 cm⁻¹. It is analogous to the compound (3) obtained upon treatment of 1,3-indandione with formaldehyde in presence of primary amines [16] (Figure 3).

Formation of this compound at elevated temperature (150°C) is understandable on the basis that 2-hydroxymethyl or 2-methylthiomethyl-1,3-indandione initially formed in this reaction can decompose at this temperature to yield (4) dimerisation of which through Diels Alder reaction gives the Spiro product (2) (Scheme 1).

4. Conclusion

Synthesis of this novel compound was confirmed by different spectral techniques. Its IR and ¹HNMR studies suggest the oxidative cyclizations involving methylene group of one indandione moiety and the carbonyl group of the other. Silica gel used for chromatographic techniques worked as

SCHEME 1

a good adsorbent and showed better resolution than other adsorbents.

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