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Synthesis and Characterization of 2-Substituted Derivatives of 1, 3-Indandione

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Abstract - Dimethyl sulphoxide –acetic anhydride reagent brings about an easy conversion of 1,3-indandione to its corresponding derivatives. At room temperature this reagent converts 1,3-indandione to ylide(2), an unusual dimer(3) and a novel dimeric condensation product(6). However, at waterbath temperature it affords a spiran(8) along with (2) &(6).

Keywords : DMSO, acetic anhydride, 1,3-indandione, spiran, ylide, Dimer.

GJSFR-B Classification : FOR Code: 030503



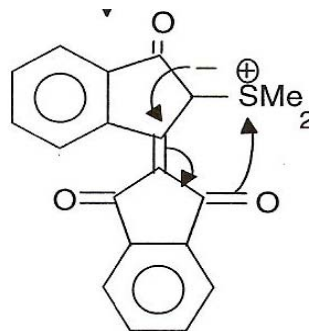
Strictly as per the compliance and regulations of :



Though this mechanism appears to be theoretically sound and logical, the literature records no reference of such dimerisation involving 1,3-diketones and activated DMSO.

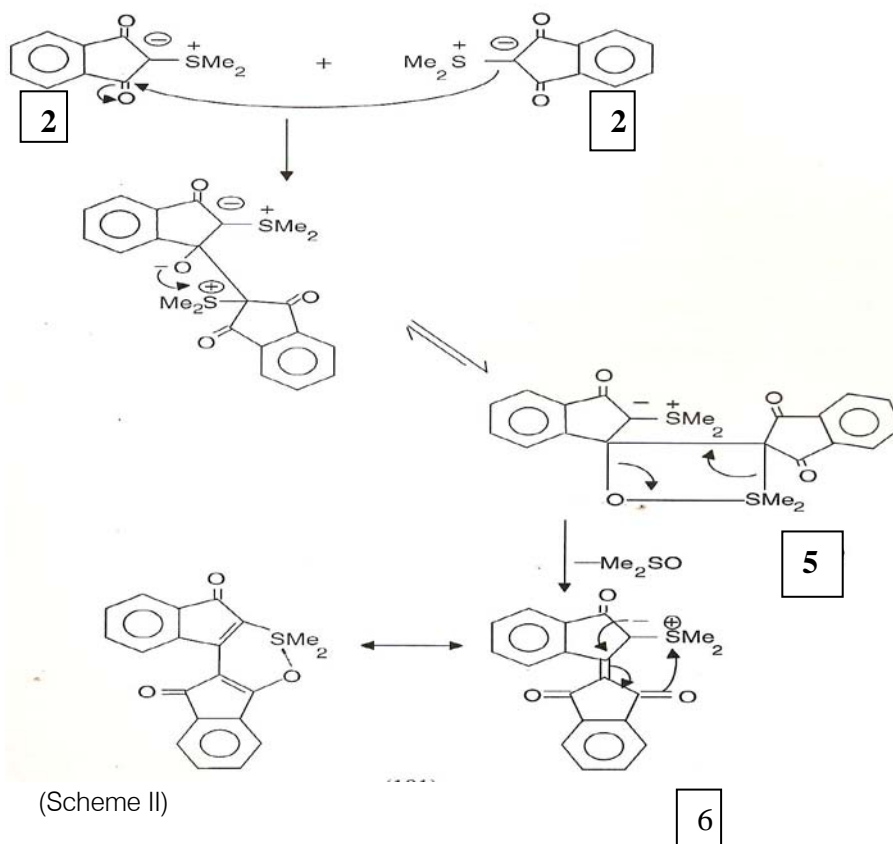
In a recent attempt when the same reaction was carried out but worked up differently i.e. through addition of excess of water and allowing it to stand as such for 24 hours, yields a colored solid which upon crystallization from chloroform pet-ether afforded a pure compound, m.p.220°C, responded positively when tested for the presence of sulphur. It was shown to have the molecular formula $C_{20}H_{14}O_3S$ on the basis of its mass spectrum showing molecular ion peak at m/z 334 and characteristic $M+1$ and $M+2$ peaks confirming presence of sulphur. It clearly indicated presence of two indandione residues. The infrared spectrum of the compound shows carbonyl bands at 1653 and 1629 cm^{-1} , indicating presence of 2-substituted indandione residues in which the carbonyls must also be α,β -unsaturated. It is pertinent to mention here that the infrared spectrum of 1,3-indandione shows two carbonyl absorption bands at 1740 and 1700 cm^{-1} and substitution at C-2 invariably shows disappearance of the carbonyl band at higher frequency. The singlet,

equivalent to six protons at δ 3.249 in its PMR spectrum can be assigned to the two methyl groups present on sulphur. The spectrum is devoid of any other signal except for the multiplets equivalent to eight aromatic protons in the region of δ 7.269-8.420. This justifies our assumption that the compound must have resulted through condensation of two indandione moieties.



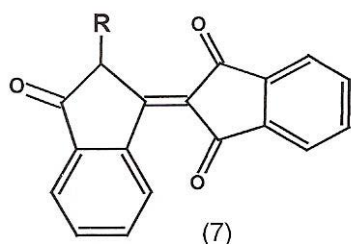
(6)

Mechanistically the carbanion of ylide (2) under the conditions attacks the carbonyl of the other moiety and the resulting four membered cyclic intermediate (5) being unstable collapses through elimination of DMSO to give a compound (6). (Scheme II)



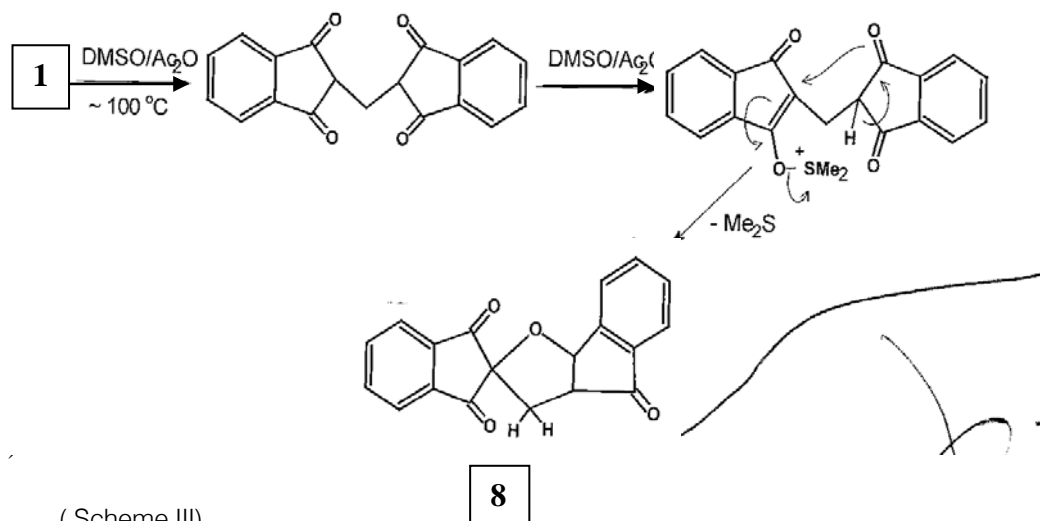
A different route for the formation of this compound can also be envisaged on the analogy of compound (7), which arises through condensation

between two indandione moieties under mild basic condition¹³.



The reaction between 1,3-indandione and DMSO-acetic anhydride reagent when carried out at

water bath temperature, reaches completion in 12 hours. Work up through removal of the reagent under vacuum followed by chromatography afforded compounds (2) and (6). The minor product, m.p. 255°C isolated from this reaction was characterized as the spiran (8). Its pmr and ir spectra showing a singlet equivalent to two protons at δ 3.01, apart from eight protons in the aromatic region and carbonyl bands at 1750 (shoulder), 1722 and 1700 cm^{-1} , are in full agreement with this structure. The mass spectrum showing M^+ at m/z 302 (base peak) and other expected fragments, confirms this. (Scheme III)



(Scheme III)

III. SPECTRAL DATA

(2) $^1\text{H NMR}(\delta)$ (CDCl_3)	3.024 (6H,s, S- (CH ₃) ₂), 7.760 – 7.946 (4H,m, Ar – H).
V_{max} (KBr)	1635 and 1595 cm^{-1}
(3) V_{max} (KBr)	3400, 1710, 1645 (weak) , 1545-1600 (broad multiplet), 1400 and 1260 cm^{-1}
Mass	m/z 290 (M^+), 148, 105, 104 (base peak) and 76.
(6) $^1\text{H NMR}(\delta)$ (CDCl_3)	3.249 (6H, s, S - (CH ₃) ₂), 7.269 – 7.740 (8H,m, Ar-H)
V_{max} (KBr),	1653 and 1629 cm^{-1}
Mass. M/z	334 (M^+), 319, 309, 272 (base peak) 202, 189, 144, 132, 104 and 76.
(8) $^1\text{H NMR}(\delta)$ (CDCl_3)	3.01 (2H,s,-CH ₂), 6.90 – 8.75 (8H,m, Ar – H)
V_{max} (KBr),	1722 (broad), 1700, 1750 (shoulders) cm^{-1}
Mass m/z ,	302 (M^+ base peak), 274, 273, 246, 218, 158, 104, 94 and 76.

IV. EXPERIMENTAL

A mixture of 1,3 indandione (1.5gms), DMSO (12ml) and acetic anhydride was kept at room temperature for three days. Workup through removal of reagent under reduced pressure afforded a solid which upon column chromatography over silica gel using benzene – ethyl acetate as eluent yielded (2) and (3). The compound (2), m.p. 165°C was found to be soluble in chloroform and responded positively when tested for the presence of sulphur and identified as ylide. The second compound (3) obtained in minimal amounts

melts at 280° dissolves only in methanol and contains no sulphur.

An identical mixture of 1,3 indandione and DMSO acetic anhydride was also kept at room temperature for 3 days but worked up in a different manner, i.e, through addition of excess of water. On standing for about 24 hours a red coloured solid separated out which was washed and dried. Crystallisation from chloroform – pet-ether afforded (6), m.p 220°C and is freely soluble in chloroform.

However, when a mixture of 1,3 indandione (2gms), DMSO (16ml) and acetic anhydride (8ml) was

maintained at water bath temperature for 12 hours and work up through removal of solvent under reduced pressure afforded red coloured solid residue. Chromatography of which over silicagel using benzene – ethyl acetate (70:30) as eluent afforded again the ylide (2), a spiran (8) in minimal amounts and (6).

V. GENERAL INFORMATION

DMSO was carefully dried according to the standard procedure. Melting points taken are uncorrected and spectral data of the compounds was recorded in RSIC Punjab University Chandigarh.

VI. CONCLUSION

In conclusion it is found that interaction of DMSO/Ac₂O reagent with 1,3-indandione leads to the synthesis of different substituted products with better yields by conventional methods. Silica gel acts as a good adsorbent. Accurate spectral data coupled with proposed mechanisms confirmed the assigned structures of different compounds.

VII. ACKNOWLEDGEMENT

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