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Dimethyl Sulphoxide-Acetic Anhydride: An Excellent Source of Formaldehyde and Thiomethanol

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The reaction between DMSO and Ac_2O at water bath temperature yield formaldehyde and thiomethanol when exposed to this modified reagent. β-diketone and β-naphthol react with formaldehyde to give corresponding methylene-*bis*-derivatives and thiomethanol acting as Micheal donor reacts with compound (3Z)-3-(2-hydroxybenzylidine)-2*H*-chromene-2,4(3*H*)-dione (**7**) to give an adduct 4-hydroxy-3[(2-hydroxyphenyl)(methylthiomethyl)]-2*H*-chromene-2-one (**9**) exposure of **7** to thiophenol give 4-hydroxy-3-[(2-hydroxyphenyl)(phenylthiomethyl)]-2*H*-chromen-2-one (**10**).

Key Words: DMSO, Acetic anhydride, Formaldehyde, Thiomethanol.

INTRODUCTION

Dimethyl sulphoxide activated by acetic anhydride converts enols into sulphur ylides, incorporates methyl thiomethyl groups in to phenols, oxidizes alcohols, induces oxidative rearrangements in certain hydroquinones[1]. In our earlier studies we have reported that interaction of this reagent with 4-hydroxycoumarin, dicoumarol[2] and 3-substituted 4-hydroxycoumarins[3] leads to mechanistically interesting products. Formation of dicoumarol during reaction of this reagent with 4-hydroxycoumarin led us to assume that formaldehyde and thiomethanol are generated during reaction of dimethyl sulphoxide with acetic anhydride, by a mechanism such as that indicated in **Scheme-I**, involving a Pummerer rearrangement made possible by prior acetylation of DMSO and its further decomposition.

EXPERIMENTAL

Melting point were taken on Koflerblock and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer. The NMR spectra were recorded on different instruments. Analyses were carried out by

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the microanalytical services, A.M.U. Aligarh. DMSO was carefully dried according to standard procedure. DMSO-Ac_2O mixture was taken in the ratio of 2:1 v/v.

Reaction of β-naphthol & 4-hydroxy 6-methyl-2*H*-pyran-2-one with pre-heated DMSO-Ac_2O

With β-naphthol: DMSO (8 mL) and acetic anhydride (4 mL) heated on a boiling water bath for 2 h and then 1 g β-naphthol was added into the mixture and heated on water bath for 5 d. Work up by addition of cold water and extraction with ether gave a gummy matter, which on purification through chromatography and crystallization from methanol gave 850 mg **6** as white prisms m.p. 190 ºC. Found: C, 83.90; H, 5.49 %. $C_{21}H_{16}O_2$ requires C, 84.0; H, 5.33 %. Spectral data: ν_{max}: (mull) 1620 and 1590 cm^{-1}. τ ($CDCl_3$, 100 MHz), 5.21 (2Hs, $-CH_2-$). m/z 300 (M^+), 281, 253, 239, 158, 157 and 144.

With 4-hydroxy-6-methyl -2H-pyran -2-one: 2.0 g 4-hydroxy-6-methyl 2H-pyran-2-one was added to 15 mL pre-heated DMSO/Ac_2O and the reaction mixture heated on a boiling water bath for 24 h, left overnight at room temperature and the crystalline material (1.6 g) that separates was filtered, washed with benzene and characterized as 3,3′-methylene-*bis*-4-hydroxy-6-methyl-2*H*-pyran-2-one (**5**) m.p. 245-500 ºC. Mixed m.p. with **5** prepared through formaldehyde method gave no depression and identity further confirmed by IR comparison.

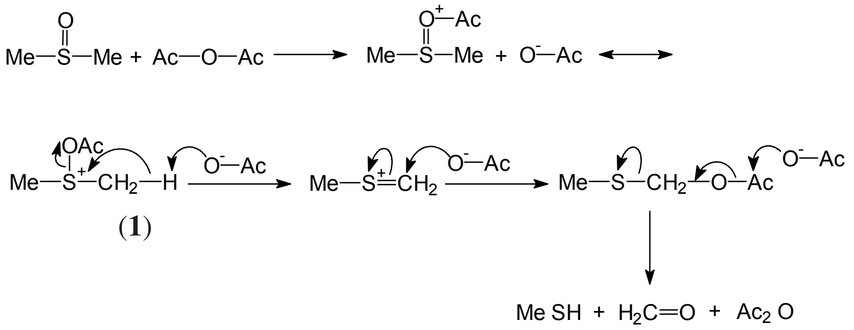
Preparation of 3-(2-hydroxy benzylidine)-2*H*-chromene-2,4-(3*H*)-dione (7): By treating 4-hydroxy coumarin with salicylaldehyde yields depending on the comparative amounts of the two starting materials.

Reaction of 7 with pre-heated DMSO-Ac_2O: DMSO (8 mL) and acetic anhydride (4 mL) was heated on a boiling water bath for 2 h. 500 mg **7** was added into the mixture and heated at water bath temperature for 7 d. The reaction mixture was poured into cold water, extracted with ether and crystallization from benzene-light petroleum gave 300 mg **9**, m.p. 140 ºC. Positive test for sulphur. Found C, 65.41; H 4.15 % $C_{17}H_{13}O_4S$ requires C, 65.17; H 4.15 %. ν_{max} (KBr) 3400, 1720, 1640 and 1620 cm^{-1}. τ ($CDCl_3$, 90 MHz) 4.98 (1HS, $-CH-SCH_3$), 8.28 (3HS, $-S-CH_3$) m/z 314 (M^+, missing), 250, 249, 222, 221, 165 and 163.

Reaction of 7 with thiophenol: To a solution of 380 mg **7** in 10 mL acetone over 300 mg anhydrous potassium carbonate was added 167 mg thiophenol. The colour of the solution changed from purple to light yellow. Removal of acetone after filteration left a light yellow oil which was washed several times with light petroleum to remove thiophenol. The residue **10** was insoluble in methanol-chloroform.

RESULTS AND DISCUSSION

The reactions of modified DMSO-Ac_2O reagent which not only confirms our earlier assumption, but can also be used as excellent sources of formaldehyde and thiomethanol under anhydrous conditions. It is found that when 2:1 mixture of DMSO and acetic anhydride is heated on boiling water bath for 2 h, the acetoxysulphonium ion (**1**) which brings about oxidation and methyl thiomethylation decomposes completely to formaldehyde and thiomethanol. Consequently when 4-hydroxycoumarin (**2**) or 4-hydroxy-6-methyl-2*H*-pyran-2-one (**3**) were added to this modified reagent and heating continued at 80 ºC, dicoumarol (**4**) and 3,3'-methylene-*bis*-4-hydroxy-6-methyl-2*H*-pyran-2-one (**5**) separated out neatly from the reaction mixture in quantitative yields.

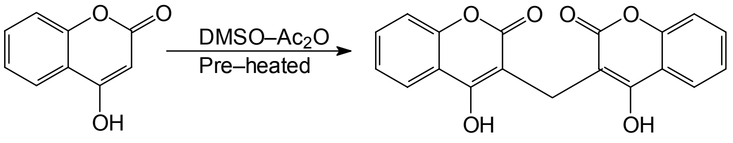


Scheme-I

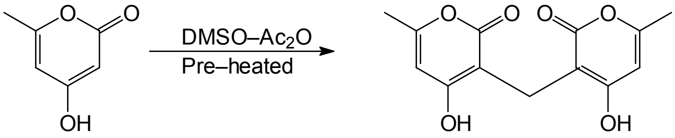
Reaction of freshly prepared DMSO-Ac_2O reagent with phenols normally gives *ortho* and *para* methylthiomethyl derivatives, but exposure of phenol, resorcinol, phloroglucinol and α-naphthol to the pre-heated DMSO-Ac_2O led to formation of phenol-formaldehyde resins, similar to those obtained up on interaction of phenols with formaldehyde. β-Naphthol, however, when maintained at 80 ºC with this reagent for 5 d, yields about 85 % of **6** identity of which was confirmed on the basis of its spectral data.

The thiomethanol is generated in the pre-heated DMSO-Ac_2O has been mentioned in our earlier studies[3]. The 3-(2-hydroxy-benzylidene)chromene-2,4-(3*H*)-dione (**7**) arising from reaction of salicylaldehyde with 4-hydroxycoumarin[4] structure of which has been corrected to 3-(3-hydroxy benzoyl)-2*H*-chromene-2-one (**8**)[5], when exposed to modified DMSO-Ac_2O not only establishes the generation of thiomethanol but also raises certain doubts about structure **8** for the compound.

Interaction of this compound with freshly prepared DMSO-Ac_2O proved too destructive to investigate. However when heated at 80 ºC for 7 d along with pre-heated reagent, and worked up by addition of water, yielded a single sulphur containing compound in 60 % yield (m.p. 140 ºC). Its infrared spectrum shows hydroxyl and carbonyl bands at 3400 and 1720 cm^{-1}, respectively, confirming presence of 4-hydroxycoumarin nucleus. In its NMR spectrum 1H singlet assigned to methine proton in the starting material at δ7.95 disappears[6] and instead shows a 1H singlet at δ5.02 along with a 3H singlet at δ1.72. Since the compound contains sulphur, the singlet at higher field must arise from S-methyl group and if on this basis structure (**9**) is allotted to the compound the 1H singlet is at the right value for the benzylic and allylic proton deshielded by sulphur. Its mass spectrum and elemental analysis data are also in full agreement with this structure.

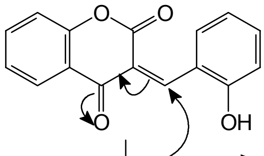


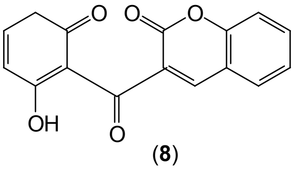
(**2**) (**4**)



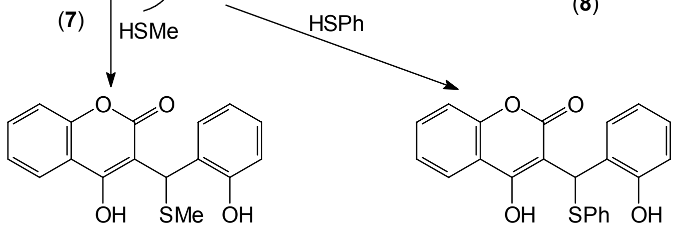
(**3**) (**5**)

(**6**)





(**7**) (**8**)



(**9**) (**10**)

Formation of this product from **8** is difficult to explain as normally it should not interact with CH_3SH at all, whereas its formation from **7** is understandable as it involves Michael addition of thiomethanol to the double bond. On this basis structure **7** appears to be correct for the compound and if at all **8** is its structure it must be either in equilibrium with **7** or under the reaction conditions isomerizes to it.

It is obvious that the preheated DMSO-Ac_2O reagent is entirely different from freshly prepared one as it lacks oxidizing properties because compounds like, **5** and **9** do not get oxidized further in it, but when kept in freshly prepared reagent, the reaction proceeds.

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