

THE REACTION OF 4-HYDROXY-2H-1-BENZOPYRAN-2-ONES WITH BUT-1,3-DIENE AND BUT-3-EN-2-OL

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Abstract - The reaction of 4-hydroxy-2H-1-benzopyran-2-ones with but-1,3-diene or with but-3-en-2-ol in presence of orthophosphoric acid afforded 3-(but-2'-enyl)-4-hydroxy-2H-1-benzopyran-2-ones. The structures of the compounds have been established spectroscopically.

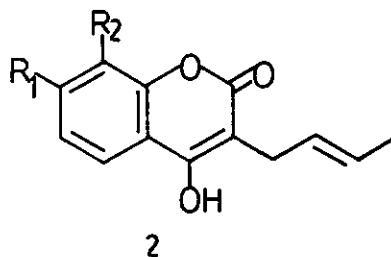
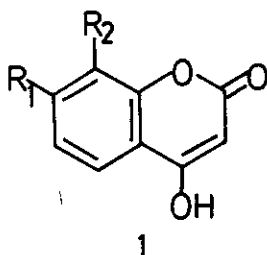
4-Hydroxy-2H-1-benzopyran-2-ones are known to react with different types of reagents¹⁻³ to give 3-substituted derivatives. It has been observed that the keto-enol tautomerism in 4-hydroxy-2H-1-benzopyran-2-ones makes the 3-position very reactive^{4,5}. In view of the above interesting reactions and their special biological properties^{6,7}, we were prompted to study the reaction of 4-hydroxy-2H-1-benzopyran-2-ones with a diene, viz. but-1,3-diene and also with but-3-en-2-ol.

A typical experiment involves the slow bubbling of but-1,3-diene into a mixture of 4-hydroxy-2H-1-benzopyran-2-one (1a) (1 g), orthophosphoric acid (85%, 1 ml) and xylene (6 ml) with constant stirring at 35-40°C for 1-2 h. Continuation of stirring for 15 h more gave a crystalline product (0.55 g), C₁₃H₁₂O₃, mp 140-141°C. It was isolated from the reaction mixture by addition of water, extraction with ether followed by purification by column chromatography and elution with benzene. In the IR(KBr) spectrum of the compound, two bands at 1610 cm⁻¹ (C=C) and 1700 cm⁻¹ (C=O) indicated the retention of the coumarin ring while band at 3200-3400 cm⁻¹ confirmed the presence of a hydroxyl group. The NMR(CDCl₃) spectrum showed a doublet centred at δ 1.71 (J=5 Hz) equivalent to three protons at C-4', another doublet centred at δ 3.40 (J=5 Hz) integrating for two protons at C-1' and a multiplet centred at δ 5.75 for two protons at C-2' and C-3' in addition to a multiplet spread over δ 7.32-7.52 and a double doublet centred at δ 7.90 corresponding to four aromatic protons in all. The above spectral data led us to assign the structure of 3-(but-2'-enyl)-4-hydroxy-2H-1-benzopyran-2-one (2a) to the product.

Similarly, condensation of but-1,3-diene with 4-hydroxy-7-methoxy-2H-1-benzopyran-

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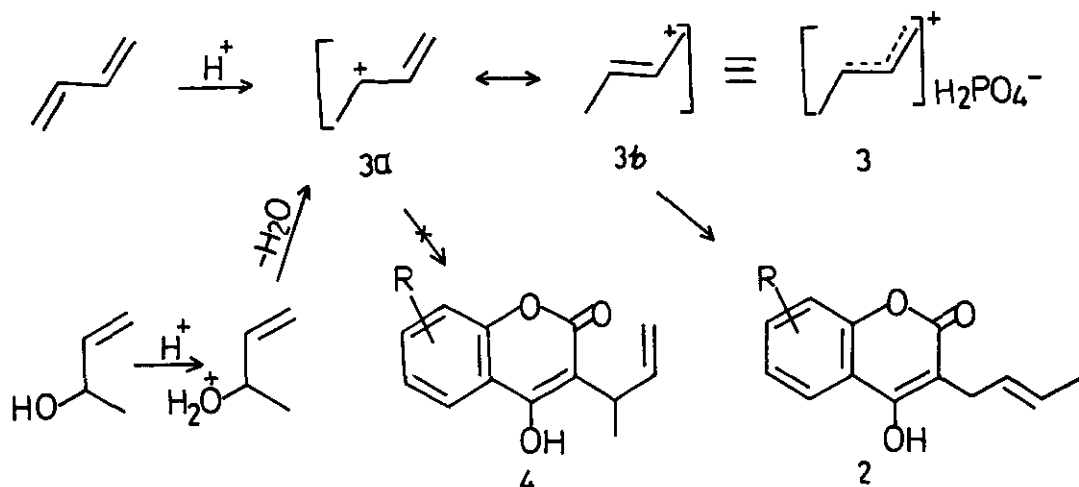
2-one (1b) gave 3-(but-2'-enyl)-4-hydroxy-7-methoxy-2H-1-benzopyran-2-one (2b) (0.55 g), $C_{14}H_{14}O_3$, mp 162-163°C; IR(Nujol): 3450-3250, 1680, 1610 cm^{-1} ; NMR($CDCl_3$) δ : 1.65(d, 3H, $J=5$ Hz), 3.25(d, 2H, $J=5$ Hz), 3.85(s, 3H), 5.65(m, 2H); 6.95(m, 2H), 8.10(d, 1H, $J=9$ Hz). A similar reaction of 4-hydroxy-7,8-dimethoxy-2H-1-benzopyran-2-one (1c) with but-1,3-diene afforded 3-(but-2'-enyl)-4-hydroxy-7,8-dimethoxy-2H-1-benzopyran-2-one (2c) (0.50 g), $C_{15}H_{16}O_5$, mp 176-178°C; IR(Nujol): 3580-3320, 1690, 1600 cm^{-1} ; NMR(acetone- d_6) δ : 1.61(d, 3H, $J=5$ Hz), 3.22(d, 2H, $J=5$ Hz), 3.85(s, 3H), 3.92(s, 3H), 5.48(m, 2H), 7.0(d, 1H, $J=9$ Hz), 7.66(d, 1H, $J=9$ Hz).



- a, $R_1 = R_2 = H$
 b, $R_1 = OCH_3$; $R_2 = H$
 c, $R_1 = R_2 = OCH_3$

However the compound 2a could also be obtained when the reaction of 1a (1 g) was carried out with but-3-en-2-ol (0.8 ml) in xylene (5 ml) in presence of ortho-phosphoric acid (1 ml) under the conditions described above (yield 0.53 g). Similar results were obtained when compounds 1b and 1c were treated with but-3-en-2-ol in the presence of acid catalyst. In view of the spasmolytic activity^{8,9} of 3-alkenylcoumarins, it will be of interest to screen the compounds, obtained above, for some physiological activities.

A plausible mechanism of the formation of 2 may involve the generation of mesomeric cation (3) (which may exist as an ion pair) by protonation of but-1,3-diene. Either of the mesomers, 3a or 3b can alkylate the 4-hydroxy-2H-1-benzopyran-2-one to give 3-(prop-1'-methyl-2'-enyl)-4-hydroxy-2H-1-benzopyran-2-one (4) or 3-(but-2'-enyl)-4-hydroxy-2H-1-benzopyran-2-one (2) respectively. But out of the two alkylated products, 2 is thermodynamically more stable and hence expected to be formed more easily. It may be appropriate to mention here that the same mesomeric cation, viz. 3 may also be formed from but-3-en-2-ol in presence of acid (acid catalysed dehydration). The various postulated steps are shown below.



The use of but-3-en-2-ol has slight advantage over but-1,3-diene in that it is a low volatile liquid while the latter is in gaseous form and also the former does not undergo the acid catalysed self condensation so easily.

All compounds analysed well for C and H.

ACKNOWLEDGEMENTS: Our thanks are due to Council of Scientific and Industrial Research, New Delhi for financial help.

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Received, 12th July, 1983