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A NEW REACTION OF ACETYLENES, THE ADDITION OF METHANOL TO 5-HYDROXYHEX-3-YN-2-ONE. SYNTHESIS OF THE "ONION FURANONE", 2-HEXYL-5-METHYL-3[2*H*]-FURANONE.

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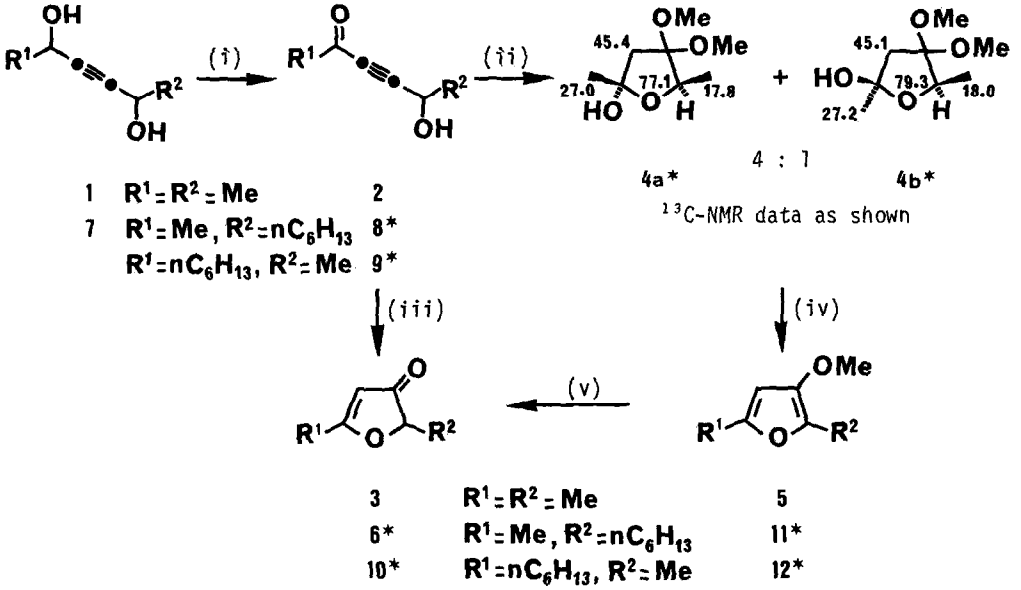
Summary. The Conversion of alkyl-substituted 4-hydroxybut-2-ynones to 2,5-dialkyl-3[2*H*]-furanones *via* 2,5-dialkyl-3-methoxyfurans is described.

The oxidation of hex-3-yne-2,5-diol (1) to 5-hydroxyhex-3-yn-2-one (2) with chromium trioxide[1a] or (better) manganese dioxide[1b] is known. Conversion of the latter (2) to 2,5-dimethyl-3[2*H*]-furanone (3) is commonly believed to require the presence of mercury, although the reaction of acid alone on the related acetals led to 3-furanones.[2] Compound (3) has also been made from diacetyl dimer by acid hydrolysis without mercury.[3]

We have prepared 5-hydroxyhex-3-yn-2-one (2) in 50% yield more conveniently by oxidation of the diol (1) with hydrogen peroxide catalysed by tungstate ion,[4] and found that (2) is converted to the furanone (3), either by acid alone, or by methoxide-catalyzed addition of methanol to the triple bond, followed by gentle heating of the intermediate acetals (4). This leads to the enol ether, 3-methoxy-2,5-dimethylfuran (5), previously made in poor yield from (3),[5] from which the furanone (3) was obtained by brief treatment with oxalic acid or an acid ion exchange resin.[6]

This sequence was followed to prepare 2-hexyl-5-methyl-3[2*H*]-furanonen (6), a constituent of onions, leeks,[7] and shallots.[8] Undec-3-yne-2,5-diol (7), made by Grignard reaction between but-3-yn-2-ol and heptanal, was oxidized (MnO_2 or $H_2O_2/WO_4^{=}$) to a (2:3) mixture of the hydroxyketones (8) (9). This mixture was cyclized with 1% aqueous sulphuric acid, and the products (6) (10) separated by chromatography on silica gel ((10) is eluted first). The methoxyfurans (11) (12) were also prepared by the action of catalytic sodium methoxide in methanol on the hydroxyketones (8) (9), and separated by preparative gas chromatography. Treatment of the separated methoxyfurans with aqueous oxalic acid gave the furanones (6) and (10), the former (2-hexyl-5-methyl-3[2*H*]-furanone (6)) having spectral data in accord with the published values.[7,8]



(i) 30% aq. H_2O_2, Na_2WO_4, H_3PO_3; (ii) 0.5% NaOMe/MeOH; (iii) 1% H_2SO_4; (iv) 120°; (v) 10% aq. $(CO_2H)_2$. All compounds had mass spectra consistent with the structures shown.

* ^{1}H-NMR data ($CDCl_3$): (4a) 1.13 (d, J 6.5, Me); 1.49 (s, Me); 2.09 and 2.23 (AB system, J 12, CH_2); 3.28 (s, OMe); 4.33 (q, J 6.5, CH).- (4b) 1.33 (d, J 6.5), 1.48, 2.10 and 2.23 (as for (4a)); 3.25 and 3.33 (OMe at different δ); 4.16 (q, J 6.5).- (6) see ref. 7, 8.- (8) 2.08 (s, 1-Me); 5.36 (t, J 7,5-H).- (9) 1.44 (d, J 7, 1-Me); 4.54 (q, J 7, 5-H).- (10) 0.88 (t, J 7);1.44 (d, J 7, Me); 4.47 (q, J 7); 5.41 (s).- (11) 1.56 (mult, 2H); 2.20 (s); 2.53 (t, J 7, 2H); 3.68 (s, Me); 5.87 (s, 1H).- (12) 1.55 (mult, 2H); 2.18 (s, 3H); 2.49(t, J 7, 2H); 3.70 (s, 3H); 5.87 (s, 1H).

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